THE INTERACTION OF CARBON DIOXIDE AND HYDROGEN ON SOLID SURFACES.

by

RANJAN BANERJEE, B. Sc., (Ind. Chem.),
A. I. I. Sc., A. R. T. C.

A T H E S I S

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Technical Chemistry Department,
The Royal Technical College,
Glasgow.

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ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

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INTRODUCTORY SECTION.

GENERAL INTRODUCTION.

The mechanism of chemical change has long engaged the attention of chemists as one of the most fundamental problems in chemistry. The familiar chemical equations that are ordinarily used to indicate the nature of a chemical reaction are merely meant to convey the overall conditions necessary for, and the nett results produced by, a reaction. The path traversed in a very large number of cases remains obscure.

Investigations into the mechanism of reactions are of particular interest and value in the field of catalytic chemistry, for only by an exact understanding of the course followed by such reactions can catalysts be scientifically used in initiating, governing and directing the path of a chemical change.

A large majority of catalytically influenced reactions are of the class which proceed at the interface between two or three phases. In such heterogeneous reactions it becomes all the more difficult to determine the mechanism, and although a large amount of work has been done on such reactions, many extremely simple reactions are being investigated to-day with a view to fuller understanding.

The subject of the investigation embodied in this thesis/

thesis, namely, the interaction of CO_2 and H_2 over a nickel catalyst to produce methane and water is usually written as:-

$$CO_2 + 4H_2 \xrightarrow[200^{\circ}C.]{Ni} CH_4 + 2\ H_2O$$

This equation suggests that a simultaneous reaction between five molecules is taking place. This is extremely unlikely. The more probable course would be a series of simple bimolecular or monomolecular reactions culminating finally in the production of only methane and water.

In such a reaction the surface on which it is occurring is obviously the important factor determining the course. The active surface of the catalyst prepares the molecules in some specific way for reaction to occur either by an increase in energy, or by local concentration in right proportions, or by a particular orientation of the reactants which determine and enhance specific chemical changes. Information as to the mechanism of a surface reaction can, therefore, only be gained by a logical correlation of several important factors. These factors are, the degree and nature of adsorption and desorption of the reactants and products shown by the catalyst surface, their ability to form and decompose possible intermediate products, the manner in which the variations in the rate of reaction occur, the order of the reaction and the various physical constants. These factors/

factors in relation to catalysis are more fully discussed in the subsequent chapters of the Introductory Section.

This thesis is concerned with some investigations into the mechanism of the interaction of Carbon dioxide and Hydrogen over promoted nickel catalysts. The subject is of fundamental importance in very many branches of industrial chemistry, particularly with regard to the formation of hydrocarbon derivatives from the oxides of Carbon.

Parts I and II of the experimental section are concerned with investigations into the kinetics of the reaction at atmospheric pressure and elevated pressures, under streaming conditions. Part III deals with some investigations into the behaviour of possible intermediates.

References to literature have been denoted by subscripts and a list of references has been provided at the end of the thesis.

Figures, graphs and tables in each section have been numbered separately.

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CHAPTER I.

HETEROGENEOUS CATALYSIS.

Catalytic reactions have been recognised since the days of the alchemists, but they were first so named by Berzelius about 1835. (1) He studied a number of chemical changes which he could not explain by theories current at that time, and suggested that those which proceeded in many cases in the presence of some specific agent, and not in its absence, were due to the action of what he called a "catalytic force." Before that, Kirchoff (2) had found that dilute acids were unchanged in the hydrolysis of starch to sugars.

Sir Humphrey Davy, in a communication to the Royal Society in January, 1837, stated that when a piece of platinum wire was warmed and plunged into a mixture of combustible gas and air or oxygen, it became incandescent and caused the gas to burn, often with explosive force. This type of reaction was further studied by Henry (3) in a series of remarkable experiments on the selective combustion of various gases in the presence of platinum.

Faraday (4) extended the observations of Davy and developed views on the mechanism of contact action, which even at present are not fundamentally modified. His ideas as expressed in those days seem very close to the modern point of/

of view that catalytic action is conditioned by a preliminary adsorption, or incipient chemical combination between the catalyst and the reactants. The consideration and classification of catalysis from an academic standpoint, however, was somewhat confused during the nineteenth century. Modern theories put forward by Ostwald (5), Armstrong (6) and many other contributors of the present century greatly clarified the position. These theories were of two distinct types, namely, those which relied on purely physical factors, and those which assumed the intermediate formation of something similar to a chemical compound. These rather divergent views were later more or less combined to give the present adsorption or unstable intermediate compound theory of the mechanism of catalytic reactions.

A catalyst may be defined as initiating or accelerating chemical change while itself remaining unchanged chemically. Its physical state, however, need not remain unaltered since it is known, for example, that platinum wire becomes pitted and spongy during the process of catalytic oxidation. Since a catalyst must normally modify the velocity of two inverse reactions to the same degree, it does not affect the final state of equilibrium in any given system; it merely hastens the attainment of that equilibrium. Apart from the function of increasing the rate of a given reaction, or as is usually the case, lowering the temperature at which

a/

a reaction will occur at a desirable rate, a catalyst may direct a reaction along a particular path when several are possible, under given conditions of temperature and pressure.

The physical theories of catalysis were first based on the fact that porous materials such as charcoal or platinum, which accelerated such reactions as the union of hydrogen and oxygen, could concentrate the gases in a layer on their surface with accompanying thermal effects. Van't Hoff (7) concluded that the gases were brought into a state of compression and abnormal concentration by the catalyst, so that chemical combination was greatly accelerated without any definite chemical reaction with the catalyst. The gaseous adsorption at this time was regarded as a layer several molecules thick at the solid surface, the rate of chemical reaction being a function of the rate of diffusion in this layer and not dependant on any actual chemical change at the catalyst surface. (8)

Sabatier (9) showed that the above view could not account for varying chemical action on a single substance by different catalysts. To take an example, formic acid was decomposed by zinc oxide into hydrogen and carbon dioxide, and by titanium oxide into water and carbon monoxide.

The simple layer theory also failed to explain why different gases should be preferentially adsorbed by different catalysts/

catalysts and why many catalysts should show selective action and produce isomeric and other changes. (10)

Purely physical concepts having failed to give a satisfactory account of catalysis, some investigators sought to explain the phenomena on a physical-chemical basis. The physical nature of adsorption was defined more clearly by the investigations of Lord Rayleigh, (11) W.B. Hardy (12) and others, but it was Langmuir who finally provided the new concept of adsorption in precise terms. (13) He suggested that adsorption on a solid surface is frequently concerned with forces similar to those in chemical valence, and since such forces are exerted over a distance of the order of $2 - 3 \times 10^{-8}$cm., only a unimolecular layer of adsorbed gas could be formed. Thus the physical or adsorption theory of catalysis approaches in this form very closely to the corresponding development of the older intermediate compound theory.

Sabatier and Mailhe (14) studied the action of a large number of metallic oxides upon ethyl alcohol vapour at 300°C., and showed that certain oxides, e.g. of manganese or tin, are almost entirely dehydrogenating in character, giving only acetaldehyde and hydrogen, whilst others - especially thoria and alumina - are entirely dehydrating, yielding ethylene and water. Others, such as uranium oxide, cause both dehydrogenation and dehydration to take place simultaneously/

simultaneously. Sabatier attributed hydrogenation to the intermediate formation of unstable hydrides, and this supported the chemical or intermediate compound theory of heterogeneous catalysis. But he only considered the possibility of the union of the hydrogen with the metal, abandoning the idea of the formation of complexes between the organic compound and the metal.

Ever since the first suggestion by Clement and Désormes (15) in 1808, the intermediate compound Theory has received a considerable amount of support for various types of reactions and catalysts. (16) Salts such as barium or calcium acetate, have been claimed as the intermediates in the conversion of acetic acid to acetone in the presence of the carbonates of the metals. The study of adsorption curves of several unsaturated oils have led Armstrong and Hilditch (17) to assume the formation of an intermediate compound between the catalyst and the organic residue in certain types of reactions. The catalytic action of iron in the formation of methane from carbon monoxide and hydrogen has been accounted for by assuming the formation of iron carbonyl. (18). Another explanation of the synthesis of methane involves the formation of the formates of the metals used as catalysts. (19)

There are several other instances of postulated intermediate compound formation. Workers in this field, however/

however, emphasized that such cases do not differ fundamentally from many other catalytic reactions in which there is no formation of an intermediate compound with a definite stoichiometric composition. In connection with this intermediate compound theory, Adkins (20) laid down the following criteria for hydrogenation catalysts:-

(i) They must adsorb and activate hydrogen.

(ii) They must adsorb and activate the hydrogen acceptor.

(iii) They must hold these two reactants in the proper ratio and space relationship.

(iv) They must desorb the desired product.

Taylor and his co-workers (21) found that metallic catalysts, for example, nickel and copper, adsorbed much less nitrogen or helium than hydrogen, and that ethylene and carbon monoxide were adsorbed to approximately the same extent as hydrogen. Later they observed that the heat of adsorption of gases such as hydrogen and ethylene was different and greater than that of such gases as nitrogen and helium.

Two distinct types of adsorption have been established and recognised as a result of the work of Taylor and others. The first of these types is the purely physical or Van der Waals adsorption which attains equilibrium quickly. It does not produce dissociation of the adsorbed molecule. It occurs at relatively low temperatures and decreases as the temperature rises.

The second type has been termed 'activated adsorption' characterised by much greater heat changes. It reaches equilibrium much more slowly and has a velocity characterised by a temperature coefficient.

'Chemisorption' occurs at high velocities when a gas reacts with a solid to form a surface compound which has very considerable stability and which in this restricted area exists in stoichiometric proportions. (22) By some authors this term is used as synonymous with activated adsorption; both involve chemical bonds and it is difficult to classify a given example.

The Catalyst Surface.

Taylor (23) showed that a catalyst prepared at a low temperature adsorbs less of a reactant after being strongly heated. This suggested that a sintering of the catalyst surface takes place as a result of which the number of active points or centres on the surface is reduced. The distribution of these unsaturated 'active centres' or fields of force was pictured by Taylor (24) in terms of peaks and valleys. The structure of a typical catalyst surface may be characterised by groups of atoms which are thrust irregularly above the normal surface of the crystals. According to this view, the points at which these isolated,

or/

or semi-isolated, atoms are supposed to be situated are the seats of catalytic activity.

Schwab and his co-workers (25) gave a modified view concerning the location of activity in the catalyst, in which the active centres of Taylor's Theory are replaced by phase boundaries. Adsorbed molecules are supposed to be 'adlineated' or collected together at phase boundaries. Microphotographical observations suggested that these boundaries were the edges of the microcrystals on the catalyst surface. This 'topochemical' theory of contact action was one of the most fruitful developments of Taylor's theory.

A 'multiplet' theory of heterogeneous catalysis has been advanced by Balandin (26) in relation to dehydrogenation catalysis and later developed. Catalytic dehydrogenation occurs when a group of surface atoms appropriately spaced and of necessary activity adsorb the reactant in a definitely oriented position. Because simultaneous action on the part of several surface atoms is postulated, the theory is called the "multiplet hypothesis." The multiplet for the dehydrogenation of a molecule may consist of two, three or more surface atoms. Balandin showed several examples correlating his theory with existing experimental evidence. In spite of criticism on the general applicability of the theory, the Russian school of investigators have continued to extend these postulates. (27)

They/

They have suggested (28) a theory of hydrogenation which requires different areas on a nickel catalyst for activation of the hydrogen and the substance to be hydrogenated. The adsorption on the active points of either type occurs according to the Langmuir concept in monolayers. The stereochemical factors in the formation of activated complexes on hydrogenation and dehydrogenation catalysts suggest that the optimum internuclear distance in the crystal lattice of the active metal may be calculated from the valency bonds and angles of the complex. On this basis several materials were suggested as catalysts for the hydrogenation of ethylene. The difference in hydrogenation activities of different planes of nickel crystals, as shown by Twigg (29), was offered as additional evidence for the theory.

In recent years increasing attention has been paid to the disposition of molecules on the catalyst surface in relation to the geometry of the surface. The suggestion was made by Porter (30) that in an adsorbed layer of molecules, the correct arrangement for a reaction with a colliding molecule may be given by orientation at the surface. The data of Germer (31) using electron diffraction methods show the presence of adsorbed molecules on a surface, but while these are found to be regularly oriented at low temperatures, they are disarranged when the temperature is raised. More

progress/

progress has been made by recent work on the reactions of hydrocarbons. In considering exchange reactions between deuterium and ethylene, Twigg and Rideal (32) have shown that when the ethylene molecule is chemisorbed on the nickel surface, the double bond is opened and attachment takes place between two carbon atoms of the double bond and two nickel atoms. It can be shown that an ethylene molecule will fit on the (110) face of a perfect nickel crystal by only a slight distortion of the normal tetrahedral angle. Sheridan(33) in investigating the polymerisation of acetylene in the presence of hydrogen on a nickel catalyst,has shown that the (110) face of the nickel crystal is suitable for the growth of a polymer from acetylene held on the 3.5 Å spacing. Such simple geometric calculations, however, can at present only be applied to very few examples, and anomalous results are obtained if attempts are made to expand them to other crystal structures, or to distorted lattices such as normally exist on the catalyst surface. (34)

Promotor Action.

The fact that the activity of a catalyst could be considerably increased by the addition of small amounts of other substances was emphasized by early patents of the Badische Anilin und Soda Fabrik. (35) Pease and Taylor (36) suggested the following definition of promotor action: 'Cases in/

in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture acts independently and in proportion to the amount present.' In explaining the effect of thoria as a promotor for nickel catalysts in the reduction of carbon monoxide, Taylor (37) suggested that it acted in three different ways: (a) by supporting existing active centres, (b) by creating additional active surfaces, and (c) by altering the proportions in which the reactants and reaction products were adsorbed. These ideas received further support from the observations of Wyckoff and Crittenden, (38) on iron catalysts containing alumina and potassium oxide. Medsforth (39) investigated the reduction of the oxides of carbon by hydrogen with supported nickel catalysts containing varying amounts of oxide promotors. He found that optimum promotor concentration varied with each substance, and in contrast to Taylor's views,he attributed promotor action to the preferential decomposition of certain postulated intermediate compounds formed during the hydrogenation of the oxides of carbon.

Detailed X-ray examination of promoted copper oxide catalysts showed no change in crystal structure with increased catalytic activity. (40) Similar results were obtained by Griffith and Hill (41) with molybdenum oxide-silica mixtures. Frolich/

Frolich, (42) however, observed an increase in the copper crystal lattice in the case of zinc/copper catalysts employed in the synthesis of methanol, and Frost (43) attributed this to the formation of a brass. On the other hand, it was found that the addition of promotors to zinc oxide for use as a methanol catalyst did not affect the crystal structure. It appears, then, that X-ray examination will reveal compound formation but not true promotor action. The earlier experiments of Wyckoff and Crittenden (44) on the crystal structure of promoted catalysts for ammonia synthesis showed that the most useful oxides for promoting effect with iron catalysts, were of the unreducible type, and would give spinels of the same cubic symmetry as Fe_3O_4, with which they would form solid solutions. Although the size of the crystal lattice was unaffected by the addition of the promotor, the growth of iron crystals was greatly diminished by its presence. In the case of cobalt and nickel catalysts used for the reduction of carbon dioxide, Schenck and Wesselkoch (45)a,found that there were clear indications of the existence of mixed crystals in the presence of effective oxides such as magnesia or alumina, and that these led to the production of carbon monoxide under conditions where the pure metals alone had no effect.

In summing up the mode of action of promotors, Griffith (46) considers that it is becoming increasingly evident/

evident that the promotor acts in one of two ways. The first of these is by its effect on the chemical composition of the surface; the second by influencing the actual lattice dimensions or the stability of the crystallites. Of these two types of action, the latter would be expected to occur more often with metallic catalysts, while with compounds such as oxides or sulphides the former process would be chiefly concerned.

The above is a brief review of certain important aspects of catalytic phenomena. Other factors like retardation, activation and kinetical considerations have been left for inclusion in subsequent chapters as and when the need arises. It is appropriate to end this chapter with a summary of C.N. Hinshelwood's Presidential Address to the Chemical Society (1947). (46)

It has now transpired that most reactions take place in a series of stages and that many are chain reactions. They are chain reactions because the intermediates are free atoms or radicals, that is to say, entities which have been formed from the primitive process of severing a bond. Now studies of many experimenters have combined to show that even in non-chain reactions, the sequence of steps by which most reactions accomplish themselves is one in which each successive member is of extreme simplicity, involving, for example, the reaction of/

of the fewest molecules, the breaking of a single bond, or the transfer of a single atom or electron from one partner to another. From a general point of view, spontaneous changes proceed with diminution of free energy, but if they are a kind whose progress can be measured, there are nearly always energy barriers separating the initial and final states. The overcoming of these barriers depends upon strong local fluctuations whereby one or both of two things may happen: (a) abnormal amounts of energy are accumulated in a few molecules, and (b) there is a momentary occurrence of unusual spatial distributions of molecules. If a great deal of energy has to be concentrated locally we speak of a high energy of activation; if many molecules have to come together or if they need to assume highly specialised positions and orientations, then we speak of a low entropy of activation.

The energy barriers in ordinary stepwise reactions would usually be unfavourable, but these are lowered when suitable receptor molecules are present and suitably disposed to take up atoms or radicals released by the breaking of bonds, and when suitable complexes are formed which obviate the need for the appearance of unnatural charges on atoms. In heterogeneous reactions, what seems to be the essential thing is that the formation of chemical links between surface atoms and adsorbed atoms or radicals allows the resolution of reactions into steps of maximum simplicity with lowered energy barriers. An important character/

character is that the active intermediates instead of being free and transient, are preserved, as it were, in a state of suspended animation until the appropriate reaction partners arrive.

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CHAPTER II.

THE REDUCTION OF CARBON DIOXIDE TO METHANE AND OTHER ALLIED REACTIONS.

The reduction of carbon dioxide by Hydrogen in the presence of metal catalysts has been the subject of a considerable amount of investigation. It has usually been considered in connection with reactions involving the hydrogenation of carbon monoxide, but has not been studied as thoroughly as the latter, because of the waste of hydrogen involved when the process is considered from the economic standpoint.

Probably the earliest investigators were Jahn (47) and Bach (48) who were interested in the action of palladium. The first reference to the catalytic synthesis of methane from hydrogen and the oxides of carbon was however, due to Sabatier and Senderens (49), and arose from the general method of direct hydrogenation evolved by them. (50) Finely divided nickel reduced at 300°C. from the oxide was used, and it was reported that hydrogenation begins at 230°C. and is complete at 300°C. It is to be noted that both of these temperatures are higher than the corresponding temperatures for the hydrogenation of carbon monoxide found by them - namely 200°C. and 250°C., respectively. Excellent yields of methane may be obtained when the reaction is carried on between 300-400°C. with an excess/

excess of hydrogen. (51) Neumann and Jacob (52) studied the equilibrium relationship of the reaction in the presence of nickel deposited on magnesia. They found that reduction began at slightly above 180°C. and reached a maximum at 328°C., corresponding to a methane yield of 95.3 per cent. Methane yield decreased above 328° and reached zero at 1020°. Above 540°C. the reaction was complicated by many secondary reactions, among them being:

$$C + CO_2 \rightleftharpoons 2CO, \quad CO_2 + H_2 \rightleftharpoons CO + H_2O, \quad CO_2 + Ni \rightleftharpoons NiO + CO.$$

Agreement was found to be poor between the observed values of the equilibrium constants of the reaction, $p\,CO_2 \times p^4 H_2 \,/\, pCH_4 \times p^2 H_2O$ and those calculated by combining the equilibrium constants of the reactions:-

$$C + CO_2 \rightleftharpoons 2\,CO$$

$$C + 2H_2 \rightleftharpoons CH_4$$

$$2(CO_2 + H_2 \rightleftharpoons CO + H_2O)$$

Ipatieff (53) studied the reaction over nickel at 450°C. and showed that in the presence of an excess of carbon dioxide (150 per cent.) there was almost complete removal of hydrogen, whereas when theoretical amounts of hydrogen were taken, a considerable amount remained unreacted. From experiments under high pressure in a bomb, he came to the following conclusions:-

(1)/

(1) In the presence of excess of hydrogen, complete reduction of carbon dioxide does not take place.

(2) In the presence of an excess of carbon dioxide, hydrogen does react.

(3) Nickel oxide and nickel are equally effective.

(4) When using concentrations of carbon dioxide and hydrogen corresponding to theoretical, the reduction reaction appears to cease at some way from completion.

In a contribution to the theory of promotor action, Medsforth (39) studied the hydrogenation of carbon monoxide and dioxide to methane over nickel and promoted nickel catalysts. He found that the addition of catalytic dehydrating agents to a nickel catalyst produced a remarkable increase in reaction velocity. With carbon monoxide it was found that the addition of ceria, thoria, glucinia, chromium oxide, alumina increased the reaction rate 12-17 times. Zirconia, molybdenum oxide, vanadium oxide increased the rate to a less extent, and metallic copper, silver and tin had no effect. There was an optimum concentration for each promotor, although it had no relationship with the molecular weight. With thoria and to a less extent with ceria, a large ill-defined region exists in which quite considerable changes in concentration produce no corresponding effect on velocity. With carbon dioxide, it was found that the promotor action of the oxides of vanadium, molybdenum, chromium, glucinium and thorium increased in the order mentioned. The optimum concentration of thoria was 10 per cent. of nickel and/

and that of glucinia, 20 per cent.

Russell and Taylor (37) studied the adsorption of carbon dioxide and hydrogen on nickel and nickel-thoria catalysts and found that although the promoted catalyst showed increased adsorption for the two gases at these elevated temperatures at which reaction occurs, the increase was in no way proportional to the increased catalytic activity.

Hightower and White (54) studied the equilibrium of methane synthesis from water gas, and mixtures of carbon dioxide and hydrogen over nickel catalysts. For a composite reaction, $CO + CO_2 + 7\ H_2 = 2CH_4 + 3H_2O$, the highest value of the equilibrium constant

$$\log_e K \left[\text{for } K = (pCH_4)^2\ (pH_2O)^3 \Big/ (pCO)\ (pCO_2)\ (pH_2)^7\right]$$

was found to be 19.6 as compared to calculated values of 19.4 - 22.4 at 350°C.

Randall and Gerard (55) while investigating the equilibrium in the reduction of carbon dioxide at various temperatures, found the following values for the equilibrium constant K $\left[\text{for } p(CH_4)\ p^2(H_2O) \Big/ p(CO_2)\ p^4(H_2)\right]$, at various temperatures:-

Temp. °K	-R ln K (R = 4.5787)
521.8	-4.41
523.6	-3.27
548.1	-15.35
574.1	-18.99
620.1	-18.73

The/

The free energy of methane calculated from these experiments was in agreement with the value found from direct synthesis from graphite and hydrogen in the same temperature range. They investigated the cause of the slight deposition of carbon on the catalyst and suggested that it could be occurring through the reaction $CO_2 + CH_4 = 2\,C + 2H_2O$, though the tendency was small. The reaction $CO + H_2 = C + H_2O$ was also possible, the CO in that case being derived from the water gas reaction in the lower parts of the catalyst chamber, rather than from the methane steam reaction. Randall and Schiffler(56) however, finally concluded that carbon was deposited by the reaction, $CO_2 + 2H_2 = C + 2H_2O$.

In 1933 Koch and Küster (57) investigated the reaction over a cobalt and nickel, "benzine" synthesis catalyst. They found the catalyst very effective even at as low a temperature as 150°C. Traces of carbon monoxide and oxygen containing compounds were found in a few cases. With a large excess of carbon dioxide, complete equilibrium was reached, which at 150-400°C. was almost completely towards the methane side. Adding steam at the start strongly retarded the reaction.

A complete study of the kinetics of methane synthesis from carbon dioxide was conducted recently by Nicolai, D'Hont and Jungers, (58) under static conditions and over a nickel catalyst. They found that both the reactants were weakly adsorbed and that

the/

the products retarded the reaction. Deuterium behaved exactly like hydrogen, although in the reduction of carbon monoxide, reaction with deuterium was faster. Hydrogenation of carbon monoxide was slower and had a higher activation energy than that of carbon dioxide. When a mixture of CO and CO_2 was hydrogenated, the CO, very strongly adsorbed, reacted completely first of all, and then the CO_2 reacted, but at a faster rate. The coefficients of adsorption 'b', of the gases at 250°C. were arranged in the following order:

$$b\ H_2 \leqslant b\ D_2 < b\ CO_2 \backsimeq b\ (CH_4 + H_2O) < b\ CO$$

i.e., carbon monoxide was most strongly adsorbed, followed by methane, water and carbon dioxide, and hydrogen and deuterium least of all.

This may be compared with the work of Fischer and Pichler, (59) who found that with nickel, cobalt and iron catalysts, the presence of CO in a CO_2 - H_2 mixture retarded hydrogenation of CO_2, while the presence of CO_2 in a CO - H_2 mixture had no influence on the yields of "benzine" obtained in the synthesis.

They also studied the conversion of CO and CO_2 to methane at high pressures. (60) Without any catalysts it was possible to reduce CO at 700°C. and 70-80 atm. pressure, and CO_2 at 600°C. and 300 atm. pressure. A number of catalysts were also used and some gave ethane in addition to methane from both CO and CO_2.

Certain/

Certain other reactions with carbon dioxide and hydrogen may now be considered.

Although equilibrium is in favour of hydrogen and carbon dioxide at low temperatures in the catalytic water gas reaction: $CO_2 + H_2 \rightleftharpoons CO + H_2O$, some reduction of carbon dioxide may occur. Bahr (61) noticed reaction at 200°C. in the presence of copper. With catalysts of copper-chromate, iron-copper, iron-cobalt and cobalt-copper-zinc and at temperatures between 200-450°C. up to 16 per cent. of carbon monoxide was obtained with mixtures of CO_2 - H_2 in the ratios 1:1 and 1:3. At slow gas flows, reduction to methane occurred, especially with catalysts containing cobalt. Hinshelwood and Pritchard (62) studied the kinetics of this reaction over platinum and tungsten at 1000°C. They found that carbon dioxide was strongly adsorbed on platinum and the rate of reaction at first increased with increase in the partial pressure of carbon dioxide, passed through a maximum and then decreased. On tungsten it was found that the adsorption of each gas was almost independent of the other. This indicated that the whole surface was not active, but that only certain parts were able to adsorb the reactants. The parts which adsorbed hydrogen were in this way different from those which adsorbed carbon dioxide. Temkin and Mikhailova (63) found that the reaction could be measured at a much lower temperature (750°K.) They observed that the rate of evaporation of adsorbed carbon monoxide was the rate governing/

governing factor. Adsorption of hydrogen was the primary step followed by reaction with an impinging carbon dioxide molecule.

The production of formic acid, aldehydes, methyl alcohol and other products from mixtures of carbon dioxide and hydrogen have also been studied by a number of investigators. Bredig and Carter (64) obtained varying amounts of formic acid by the electrolytic reduction of carbon dioxide at 70-95°C. and under about 60 atm. pressure, using several electrodes and electrolytes. Farlow and Adkins (65) obtained formic acid in the presence of amines and "Raney nickel" at 80°C. or less, in a bomb under pressures of 200-400 atmospheres.

Ipatieff and Monroe (66) prepared methyl alcohol in excellent yields from carbon dioxide. They used copper-alumina catalysts and worked at 282-487°C in the pressure range of 117-410 atmospheres. Copper alone, and alumina alone, had no catalytic effect. The most active catalysts had a copper content of 8-28 per cent., giving conversions of 94 per cent. at 410 atm. and 285°C. Carbon monoxide under the same conditions gave only 40 per cent. conversion. A reaction mechanism was suggested. The first step was considered to be the primary reduction of carbon dioxide to carbon monoxide. The next step would be the formation of formaldehyde which could be hydrogenated straight away to methyl alcohol, or the formaldehyde/

formaldehyde in the presence of amphoteric aluminium oxide could by means of intermolecular oxidation and reduction, give methanol and formic acid (Cannizzaro reaction) in the sense of the equation: $2\ HCHO + H_2O \rightarrow CH_3OH + HCOOH$. The suggestion that carbon monoxide is the first intermediate, seems to be contrary to the observation that carbon monoxide is not as readily converted to methanol as carbon dioxide.

According to a recent Japanese patent (67), higher alcohols have been synthesised from carbon dioxide - hydrogen mixtures at 400°C. and 150 atm. pressure. A mixture of the hydroxides or oxides or carbonates of manganese, zinc, iron, copper or chromium, together with the oxides or carbonates of alkali metals, supported on Kieselguhr, was used as a catalyst.

In 1936 Fischer and his co-workers (68) synthesised higher hydrocarbons from carbon dioxide. They found that ruthenium as a catalyst for the reduction of carbon dioxide was superior to any other material and that reduction set in at 100°C., but at these low temperatures only methane was formed. The reaction changed, however, when small quantities of alkali (e.g. 2 per cent. K_2CO_3) were added. The temperature of incipient reduction was thereby raised to 150°C. and beginning at 170-80°C., there were formed not only methane, but also higher gaseous and liquid hydrocarbons and oxygenated products. The most favourable temperature range was 200-225°C. Although higher /

higher hydrocarbons could still be detected at 300°C., above this temperature only methane was formed. Small quantities of alkali (0.5 per cent. K_2CO_3, 1.5 per cent. Na_2CO_3, 3 per cent. Li_2CO_3) were not sufficient to impart an oil producing power to the catalyst. Rubidium carbonate (3.4 per cent.) had the same effect as potassium carbonate. It was believed by Fischer that the higher hydrocarbons were being formed through the intermediate formation of carbon monoxide. From analogy with the metals of the iron group, it was suggested that the catalyst was a carbide although no ruthenium carbide was known.

The Mechanism of Methane Synthesis from Carbon Dioxide and Hydrogen.

Medsforth (39) proposed that in the formation of methane from both carbon dioxide and carbon monoxide, an intermediate complex of the methyl alcohol type is formed with the nickel catalyst, which is later dehydrated to give methylene radical and water and the methylene hydrogenated immediately to methane:

$$CO + 2H_2 \rightarrow H_2C.HOH \rightarrow \underset{+H_2O}{:CH_2} \rightarrow CH_4$$

The alcohol is decomposable in two ways:-

$$H_3C.OH \rightarrow 2H_2 + CO \quad \ldots\ldots\ldots (1)$$

$$H_3C.OH \rightarrow :CH_2 + H_2O \quad \ldots\ldots\ldots (2)$$

Nickel here functions also as a dehydrogenating agent, but promotors like thoria, being good dehydrating agents will by/

by increasing the rate of dehydration suppress the dehydrogenation.

The hydrogenation of carbon dioxide was treated in a similar manner.

$$CO_2 \longrightarrow H_2C\begin{matrix}OH\\OH\end{matrix} \longrightarrow CH_2O \longrightarrow CH_3OH \begin{matrix}\nearrow :CH_2 \rightarrow CH_4\\ \searrow CO + 2H_2\end{matrix}$$

This was held to explain the presence of carbon monoxide found by various workers when a large excess of hydrogen is not used. It was also suggested that a simpler hydrogenation than that shown above takes place, giving a compound of the formic acid type which is dehydrated to give carbon monoxide and water.

$$Ni + CO_2 + H_2 \longrightarrow Ni\ (HCO.OH) \rightarrow Ni + H_2O + CO$$

It is also stated that if a mixture of one part of methyl alcohol plus three parts of hydrogen (i.e., the proportion in which they would be present assuming alcohol formation) be passed over nickel, the rate of decomposition of the alcohol into carbon monoxide and hydrogen will be far greater than that of the formation of methane. However, with thoria present the rate of production of methane is fourteen times that of nickel alone. No data have been shown or referred to.

Suggestions similar to the above have also been made in the case of the reaction $CO + H_2O = CO_2 + H_2$. Wieland (69) postulated/

postulated the intermediate formation of formic acid in the reaction and this view was supported by Armstrong and Hilditch, (70) who advanced the theory that the effectiveness of copper as a catalyst in this reaction was due to the power of dehydrogenating formic acid: $CO + H_2O \rightarrow HCO.OH \longrightarrow CO_2 + H_2$. The Badische Co., used nickel as a catalyst, which decomposes formic acid rapidly at low temperatures. The presence of a hydrating agent like alumina or thoria in combination with nickel, was considered to accelerate the velocity of the reaction by forming the intermediate compound, formic acid, for decomposition by the nickel.

Armstrong and Hilditch (71) in discussing the specificity of catalytic hydrogenation, considered the route taken in methane synthesis. They observed that the possible sequence of stages, $CO \rightarrow CH_2O \rightarrow CH_3OH \rightarrow CH_4$ seemed never to have been realised and that it was almost certain that neither formaldehyde nor methyl alcohol was even transitorily produced. Similarly, according to their experience, neither of these compounds nor carbon monoxide was produced during the hydrogenation of carbon dioxide to methane; Taylor (72) however, had reported small amounts of carbon monoxide in methane produced in industrial plants from carbon dioxide. Apart from this last observation, all evidence seemed to point to a direct route.

In/

In commenting upon Medsforth's explanation of methane synthesis, Ipatieff (53), p. 535 observed that if it was agreed that the first phase consisted in the reaction of carbon monoxide with hydrogen to give formaldehyde and then methyl alcohol, the latter phase of the reaction under the influence of a dehydration catalyst should lead to the formation of methyl ether which is quite stable even at 520°C. (i.e., $2CH_3OH \rightarrow H_2O + CH_3.O.CH_3$). He proposed, as an alternative, that the methanol first formed combines with the alumina hydrate to form an ester, which under the influence of a strong hydrogenation catalyst gives methane:

$$AlO(OH) + CH_3OH = AlO(OCH_3) + H_2O$$

$$AlO(OCH_3) + H_2 = AlO(OH) + CH_4$$

Since then the subject has not been considered in great detail, until the publication of two recent reviews by Pichler (73) on the formation and decomposition of formic acid and formates and the route followed in the hydrogenation of carbon dioxide. He considers that the hydrogenation of the two oxides of carbon takes place in fundamentally different ways and that only in the case of primary reduction to carbon monoxide, are higher hydrocarbons and alcohols obtained from carbon dioxide. The hydrogenation of carbon dioxide will ordinarily lead to aliphatic compounds with one carbon atom only. Before considering Pichler's arguments, it is necessary to/

to survey the mechanism of the "Fischer-Tropsch" synthesis. Almost all investigators of this reaction are agreed that methylene groups must be produced on the catalyst surface which, under suitable conditions, will polymerise to form higher hydrocarbons. The way in which these methylene groups are produced has been the subject of some controversy. Craxford(74) and Craxford and Rideal (75) along with other investigators agree with Fischer and co-workers (76) that the first step is the formation of metal carbides. Craxford wrote the primary reaction as $2\ Co + CO + H_2 = Co_2\ C + H_2O$. Matsumura (77) however preferred to postulate the transient existence of metal oxide. It has lately been emphasised (78) that the intermediate is to be regarded as a 'surface carbide' or an array of chemisorbed carbon atoms rather than the bulk metal carbide itself. That bulk carbide is not an intermediate has now been confirmed by Kummer, De Witt and Emmett (79), who used radioactive carbon as a tracer. Weller (80) has considered the role of bulk carbide as yet undetermined. Craxford and Rideal (75) postulated that the next step was the formation of methylene groups with molecular hydrogen; their work on the ortho-para-hydrogen conversion over synthesis catalysts showed that whenever atomic, or chemisorbed hydrogen was present only methane was produced. Matsumura (77) argued that this coincidence does not necessarily mean that methylene cannot be produced by reaction/

reaction with atomic hydrogen produced by activated adsorption on the surface. Indeed, such participation of active hydrogen is very probable as synthesis temperatures coincide with those of maximum amount of activated adsorption of hydrogen. The o-p hydrogen conversion does not proceed to an appreciable extent during synthesis because most of the catalyst surface is covered with polymethylene groups. The absence of higher hydrocarbon formation during the initial period of operation is to be explained by assuming that a certain considerable time is required to cover the catalyst surface with polymethylene groups and slow up the reduction of methylene to methane. Predominant methane formation at temperatures above 250°C. is due to rapid desorption of methylene groups which are then presumably reduced in the gas phase.

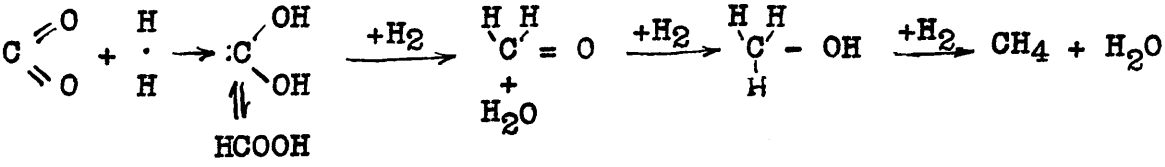
Ei'dus and Zelinskii (81) considered cobalt carbide to be neither an intermediate nor a catalyst in the synthesis process, although they confirmed the formation of methylene radicals. Zelinskii (82) further postulated that intermediate carbide formation plays a role only on iron catalysts and not on cobalt and nickel. The synthesis reaction is supposed to proceed by way of the intermediate radical CHOH and $CHOH + H_2 \longrightarrow H_2O + :CH_2$. This is similar to Storch's suggestion (83) that something analogous to an "oxo"-type of reaction probably occurs at the surface. The name "oxo" reaction was given to a process developed in Germany in 1944,

by/

by which olefins were made to react with hydrogen and carbon monoxide in the presence of cobalt catalysts and at elevated pressures, to produce aldehydes having one carbon atom more than the olefins. These aldehydes could then be hydrogenated to give alcohols. Storch suggested that during the Fischer-Tropsch synthesis a similar reaction takes place. Possibly the first product is formaldehyde, which is reduced to a methylene group and subsequent addition of CO and H_2 to this would yield methyl alcohol and so on.

Another intermediate which has been suggested is Ketene, CH_2CO. This possibility was originally suggested by Elvins and Nash (84) and was later investigated by Warner, Derrig and Montgomery. (85)

Pichler's postulate about the hydrogenation of carbon dioxide may now be considered. He suggests that it takes place by way of formic acid, formaldehyde, methanol and then to methane:-



The first step in the process is the formation of atomic hydrogen. It can be formed by chemisorption on the catalyst surface, as has been shown by many investigators. Craxford (loc.cit.) has pointed out that during Fischer-Tropsch synthesis very little atomic hydrogen is present and since carbon/

carbon dioxide in the presence of large quantities of carbon monoxide remains unaffected during synthesis, atomic hydrogen seems to be essential for the hydrogenation of carbon dioxide. Formic acid can then be looked upon as the first intermediate. This is mainly produced in the unstable isomeric form of dioxymethylene. The possibility of such an isomeric change of formic acid with a labile structure, has been shown by Seshadri (86) and Pandalai. (87) The formation of formic acid itself from carbon dioxide has been achieved by a number of workers. (88) (64) (65). The next step on addition of a hydrogen molecule or two hydrogen atoms, will result in the formation of formaldehyde and water. Formaldehyde has been found in the decomposition of formic acid and formates, (95) (96) as well as in the formation and decomposition of methanol. Methanol would then be formed and subsequently hydrogenated to methane and water.

Pichler concludes that since atomic hydrogen is necessary for the hydrogenation process, it should proceed according to the above scheme and contrary to the hydrogenation of carbon monoxide, not lead to any compounds with more than one carbon atom. When higher compounds are formed, the reaction proceeds through the primary conversion to the monoxide.

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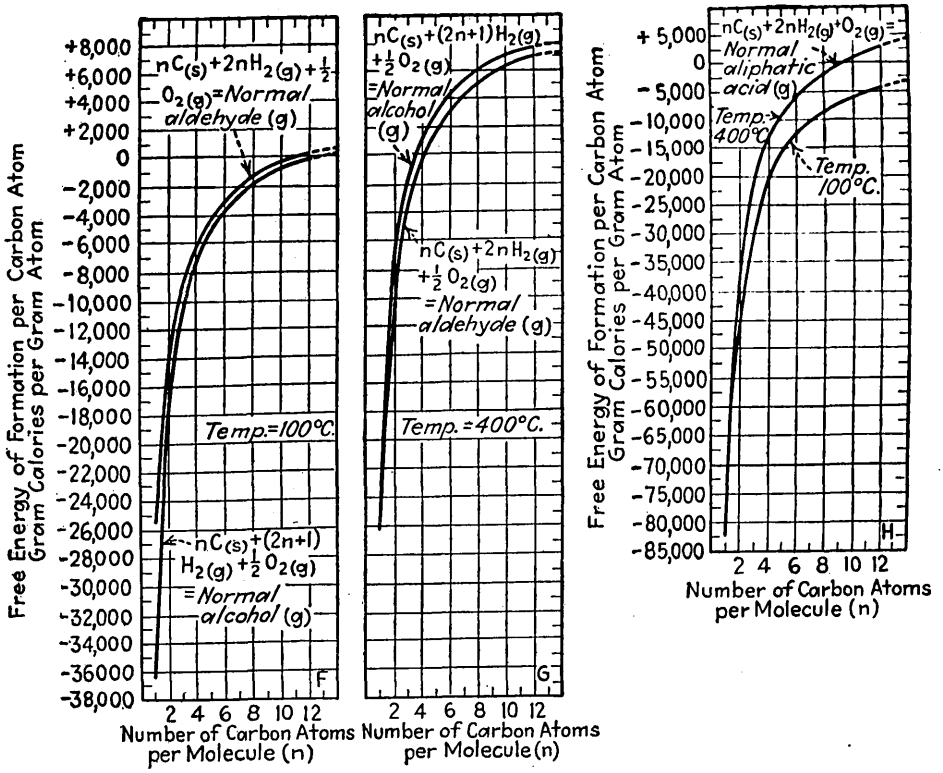
CHAPTER III.

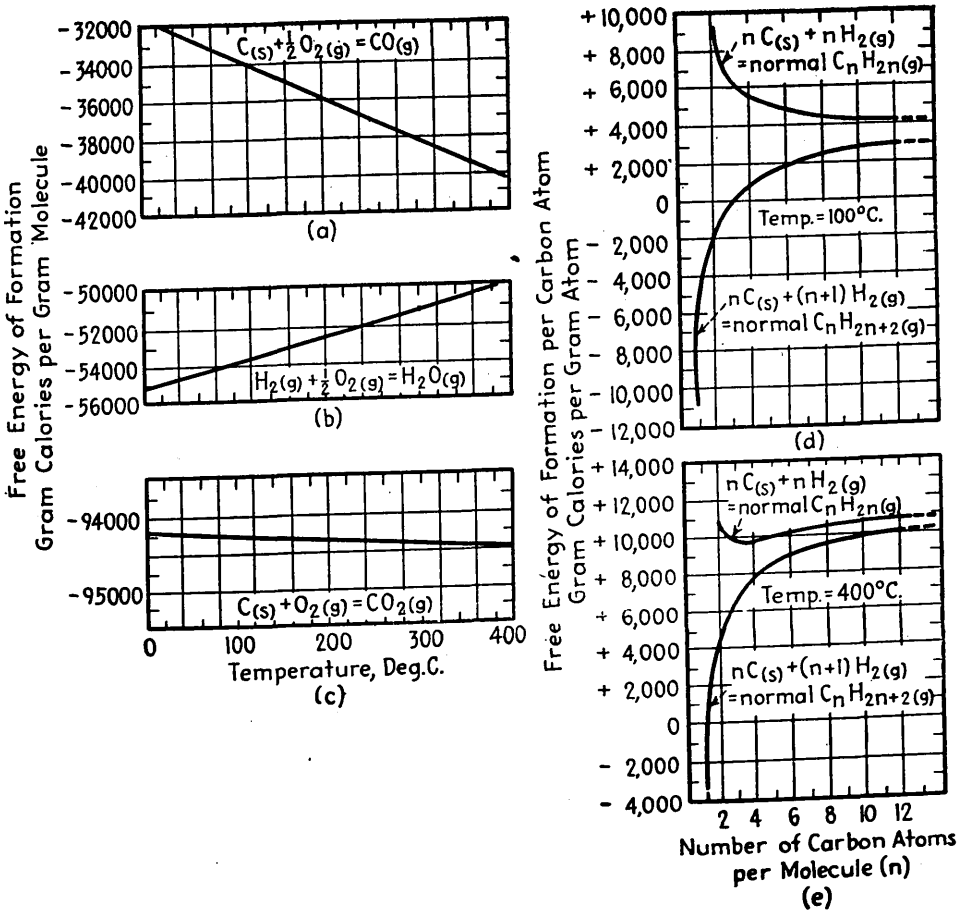
SOME PHYSICAL FACTORS OTHER THAN CATALYSTS AFFECTING THE HYDROGENATION OF CARBON DIOXIDE.

Catalysts are supposed to affect only the rate or speed of a reaction and have nothing to do with the inherent tendency of a reaction to proceed. It is therefore of importance to know whether or not a reaction is at all possible for the given conditions of temperature and pressure. The free-energy change of a specific reaction is a quantitative measure of chemical forces involved and shows the tendency of the reaction to proceed spontaneously. It is fortunate that in the relatively simple molecular problem under review, fairly reliable data for free energies are available. (89) The accompanying figure gives free-energy values of the relevant compounds. (97)

The values are for the free-energy of formation in the gaseous state at one atmosphere pressure, from the elements. For some of the compounds, values are given for 100°C. and 400°C., it being permissable to make linear interpolation between these two temperatures for intermediate temperatures. For the normal aliphatic hydrocarbons, aldehydes, alcohols and acids, the free-energy content per carbon atom is plotted. The ordinate values must be multiplied by the number of carbon atoms in the compound to obtain the molal values.

The well-known relationship $-\Delta F = 4.57\ T \log K$ exists when all the reactants and products are in the gaseous state at a partial pressure of one atmosphere. The term $-\Delta F$ is the free energy/


Free Energy of Formation per Carbon Atom Gram Calories per Gram Atom
+8,000
+6,000
+4,000
+2,000
0
-2,000
-4,000
-6,000
-8,000
-10,000
-12,000
-14,000
-16,000
-18,000
-20,000
-22,000
-24,000
-26,000
-28,000
-30,000
-32,000
-34,000
-36000
-38,000
nC(s)+2nH2(g)+½ O2(g)=Normal aldehyde (g)
Temp.=100°C.
nC(s)+(2n+1) H2(g)+½ O2(g) =Normal alcohol (g)
F
2 4 6 8 10 12
Number of Carbon Atoms per Molecule (n)
nC(s)+(2n+1)H2(g) +½ O2(g) =Normal alcohol (g)
nC(s)+2nH2(g) +½ O2(g) =Normal aldehyde (g)
Temp.=400°C.
G
2 4 6 8 10 12
Number of Carbon Atoms per Molecule (n)
Free Energy of Formation per Carbon Atom Gram Calories per Gram Atom
+ 5,000
0
- 5,000
-10,000
-15,000
-20,000
-25,000
-30,000
-35,000
-40,000
-45,000
-50,000
-55,000
-60,000
-65,000
-70,000
-75,000
-80,000
-85,000
nC(s)+2nH2(g)+O2(g)= Normal aliphatic acid (g)
Temp. 400°C
Temp. 100°C.
H
2 4 6 8 10 12
Number of Carbon Atoms per Molecule (n)


Free Energy of Formation Gram Calories per Gram Molecule
-32000
-34000
-36000
-38000
-40000
-42000
C(s)+½ O2(g) = CO(g)
(a)
-50000
-52000
-54000
-56000
H2(g)+½ O2(g) = H2O(g)
(b)
-94000
-95000
C(s)+O2(g) = CO2(g)
0
100
200
300
400
Temperature, Deg.C.
(c)
Free Energy of Formation per Carbon Atom Gram Calories per Gram Atom
+10,000
+ 8,000
+ 6,000
+ 4,000
+ 2,000
0
- 2,000
- 4,000
- 6,000
- 8,000
- 10,000
- 12,000
nC(s)+nH2(g) =normal CnH2n(g)
Temp.=100°C.
nC(s)+(n+1) H2(g) =normal CnH2n+2(g)
(d)
+14,000
+12,000
+10,000
+ 8,000
+ 6,000
+ 4,000
+ 2,000
0
- 2,000
- 4,000
nC(s)+nH2(g) =normal CnH2n(g)
Temp.=400°C.
nC(s)+(n+1) H2(g) =normal CnH2n+2(g)
2 4 6 8 10 12
Number of Carbon Atoms per Molecule (n)
(e)

energy decrease in calories for the reaction as it proceeds from left to right and represents the difference in free-energy content of all the reactants and products, T is the temperature in degrees Kelvin, and K the equilibrium constant, with the products appearing in the numerator and the reactants in the denominator in terms of individual partial pressures in atmospheres. The free energy values of all elements in their normal state at 1 atm. pressure and at any temperature are arbitrarily assigned the value of zero.

The free energy content of all compounds will in this way have either plus or minus values, since the free-energy content at any temperature is merely the free-energy of formation from the elements at that temperature.

All spontaneous reactions, i.e. those proceeding of their own accord, in the absence of any outside influences, e.g. electrical or magnetic, are attended by a free-energy decrease. If a reaction involves only one compound and an element, e.g. hydrogen, yielding as the product only one other compound of the same number of carbon atoms, then the compound with the lower free-energy is the more stable of the two under the experimental conditions chosen. Thus it is seen that the normal paraffins at 100°C. have lower free energy values than the normal olefins, i.e., at this temperature, all normal olefins are capable of being hydrogenated to normal paraffins with good equilibrium yields. Similarly, in the case of aldehydes and alcohols, it is/

is seen that at 100°C. the normal alcohols have lower free-energy values than the corresponding aldehyde. Hydrogenation is therefore possible if catalysts can be found to effect the reduction with reasonable speed. At higher temperatures, e.g. 400°C., the aldehyde is seen to possess a lower free-energy value than the alcohol. In other words, the normal spontaneous tendency at this temperature is for the alcohols to dehydrogenate to yield aldehydes. Certain other reactions may now be considered. The simplest reduction of carbon monoxide at 400°C. is:

$$CO(g) + 3\ H_2(g) = CH_4(g) + H_2O\ (g)$$

$$-40,500 + 0 + \Delta F = -3,600 - 50,000$$

$$\Delta F = -13,100 \text{ Cal. at } 400^{\circ}C.$$

This free-energy decrease at this temperature, shows that reduction of carbon monoxide is a very complete reaction as judged by the equilibrium yield that is possible. Instead of the complete hydrogenation of carbon monoxide, the partial reduction to methanol could be considered.

$$CO\ (g) + 2H_2(g) = CH_3\ OH(g)$$

$$\Delta F = -2,500 \text{ Cal. at } 100^{\circ}C.$$

This free energy decrease indicates that the reaction is possible at 100°C., but so far, no catalysts have been found sufficiently active to bring about reaction at this low temperature. If reaction occurs it is carried to methane. To get increased reaction rate, it is logical to raise the temperature. The free energy/

energy increase at 400°C. is found to be + 14,300 Cals. The above reaction is thus not capable of proceeding to any practical extent at this temperature. However, the free-energy values given are for reactants and products at 1 atmosphere partial pressure. Since the synthesis of methanol is accompanied by a decrease in the number of gaseous moles, then the equilibrium yield which is negligible at 400°C. and low pressures, can be raised to an appreciable value by working at high pressure. Equilibrium data for this synthesis from CO and H_2 are as follows:- (98)

$$K_p = \frac{P\ CH_3\ OH}{PCO \times P^2\ H_2}$$

Temp. °C.	K p
100	3.0×10
260	1.2×10^{-3}
300	1.6×10^{-4}
340	2.9×10^{-5}
380	6.3×10^{-6}

It is to be noted that K p decreased with temperature. At atmospheric pressure and room temperature methanol is perfectly stable, whilst at 300°C. it exists in equilibrium with the theoretical proportions of hydrogen and carbon monoxide to the extent of less than 2 per cent.

On the other hand, by calculation the equilibrium favours

almost/

almost 100 per cent. methanol at 300°C. under a pressure of 1000 lbs/sq.inch. With most sensitive catalysts moreover, it is necessary to use considerably higher pressures to favour the formation of methanol and reduce the possibility of side reactions.

The Fischer-Tropsch process for the synthesis of hydrocarbons higher than methane from water-gas at atmospheric pressure, can be analysed in a similar manner from available data. It is found that such reactions are entirely possible even at atmospheric pressure and temperatures up to 400°C. It must be borne in mind, however, that the higher molecular weight hydrocarbons which are formed, are likely to be further reduced to methane, since methane is the most stable hydrocarbon at temperatures near 400°C. This destructive hydrogenation or hydrogenolysis would be more apt to occur at high temperatures, for here all reaction velocities are increased, and the specific action of a catalyst is in general reduced markedly. (97) Temperature control has been found to be an important factor in this process.

Turning to the problem under review, it is in the same way possible to calculate the free energy change at various temperatures for the reduction of carbon dioxide and allied reactions. Table I gives the free energies of the various compounds and Table II the free energy change of the various possible reactions under consideration.

TABLE I/

TABLE I.

Substance.	ΔF Kgm. Cals/gm. mole.			
	100°C.	250°C.	300°C.	400°C
$CO_2(g)$	-94.26	-94.35	-94.40	-94.50
CO (g)	-33.75	-37.20	-38.00	-40.20
$H_2O(g)$	-53.90	-51.90	-51.55	-50.00
$CH_4(g)$	-10.90	- 7.25	- 6.06	- 3.60
HCOOH(g)	-82.50	-82.50	-82.50	-82.50
$CH_3OH(g)$	-36.50	-31.35	-29.50	-26.20
HCHO(g)	-25.50	-25.85	-26.00	-26.20

TABLE II/

TABLE II.

No.	Reaction ⟶	ΔF K. - Cals. 100°C.	250°C.	300°C.	400°C.
1.	$CO_2+H_2 = HCOOH$	+11.76	+11.85	+11.90	+12.0
2.	$CO_2+2H_2= HCHO+H_2O$	+14.86	+16.25	+16.42	+18.3
3.	$CO_2+3H_2= CH_3OH+H_2O$	+ 3.86	+11.10	+13.35	+18.5
4.	$CO_2+4H_2= CH_4+2H_2O$	-34.44	-16.75	-14.76	- 9.0
5.	$HCOOH+H_2=HCHO+H_2O$	+ 3.10	+4.75	+4.95	+ 6.30
6.	$HCOOH+2H_2=CH_3OH+H_2O$	- 7.90	-0.75	+1.45	+ 6.50
7.	$HCOOH+3H_2=CH_4+2H_2O$	-36.20	-28.55	-26.66	-21.10
8.	$HCHO+H_2 = CH_3OH$	-11.0	- 5.50	- 3.5	0 or +0.2
9.	$HCHO+2H_2= CH_4+H_2O$	-39.30	-33.30	-31.61	-27.40
10.	$CH_3OH+H_2= CH_4+H_2O$	-28.30	-27.80	-28.11	-27.60
11.	$HCOOH = CO_2+H_2$	-11.76	-11.85	-11.90	-12.0
12.	$HCOOH = CO +H_2O$	-5.15	- 6.60	- 7.05	- 7.70
13.	$HCHO = CO +H_2$	-8.25	-11.35	-12.0	-14.0
14.	$CH_3OH = CO+2H_2$	+ 2.75	- 5.85	- 8.50	-14.2
15.	$CH_3OH = HCHO+H_2$	+11.0	+5.50	+3.50	9.0
16.	$CO+3H_2 = CH_4+H_2O$	-31.05	-21.95	-19.61	-13.4
17.	$CO_2+H_2 = CO+H_2O$	+ 6.61	+ 5.25	+ 4.85	+ 4.3

It must be noted that the accuracy of the values in Table I depends on the accuracy of the accompanying figure. Values slightly different from these have been calculated by some investigators. For instance, Francis (90) gives the following expression for the temperature range 500-700°K, $\Delta F = -52,450 + 29\ T$ for methanol. If that is correct, the value $\Delta F_{300°C.} = -35.85$ K.-Cals. is obtained, which is considerably higher than the value -26.0 K.-Cals. given in Table I. In the case of methane, however, better agreement is obtained. Francis gives the expression $\Delta F = -20,000 + 26.2\ T$ for the temperature range 700-1000°K., but observes that it can be used for lower temperatures as well. According to this expression, $\Delta F_{100°C} = -10.24$ and $\Delta F_{400°C.} = -2.4$ K.-Cals. These values are slightly lower than the corresponding values -10.9 and 3.6 K.-Cals. respectively, shown in Table I. However, accepting the values of Table I as correct, the free energy change in the different reactions have been drawn up in Table II.

It will be noted from equations 1. to 3. that the formation of formic acid, formaldehyde or methanol direct from CO_2 and H_2, are not spontaneous reactions, and therefore cannot occur to any extent under atmospheric pressure and the temperature range chosen. Only high pressures and special catalysts could bring these changes about, since they are all accompanied by a reduction in volume. Of the various ways in which formic acid could be hydrogenated, that to formaldehyde,

equation 5 is not spontaneous. Equation 6 is possible at lower temperatures but is reversed above about 250°C. Direct hydrogenation to methane is however accompanied by a large decrease in free energy. Equations 8, 9 and 10 show that the reduction of formaldehyde and methanol are spontaneous reactions.

For a step reaction to take place, each of the steps must necessarily be spontaneous. (91) Thus, thermodynamically at least, it appears that the first step in the reduction of carbon dioxide, resulting in the formation of formic acid, is unlikely at atmospheric pressure. However, under the influence of the catalyst surface it may be possible that some compound of the nature of formic acid is formed, which is hydrogenated to a compound of formaldehyde type and once these two steps have been accomplished, the rest could follow spontaneously.

If the alternative proposal of a primary reduction to carbon monoxide is considered, it will be noted from equation 17 that this reaction is also not spontaneous at the temperatures mentioned, but shows a greater probability than equation 1. Once carbon monoxide is produced, the tendency of the reaction would be to proceed via the intermediate production of methylene, rather than via the formation of formaldehyde and methanol. This would be specially so in the case of a nickel or cobalt catalyst as has been indicated in the investigations on Fischer-Tropsch catalysts.

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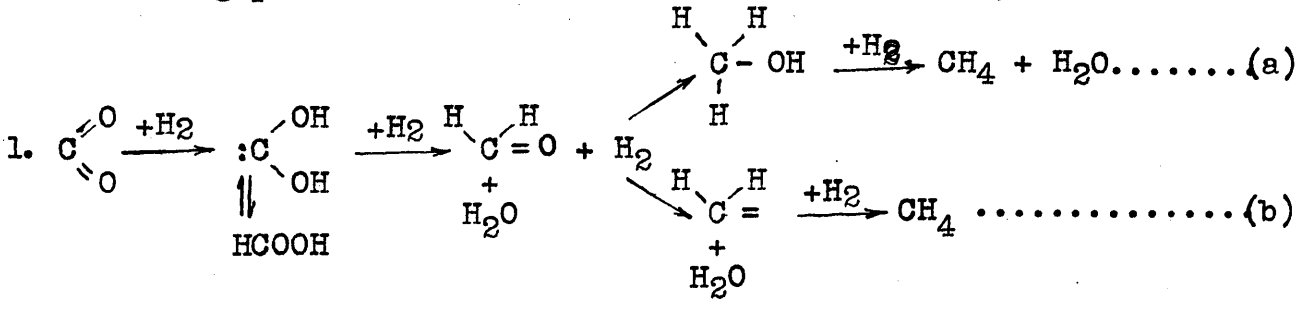
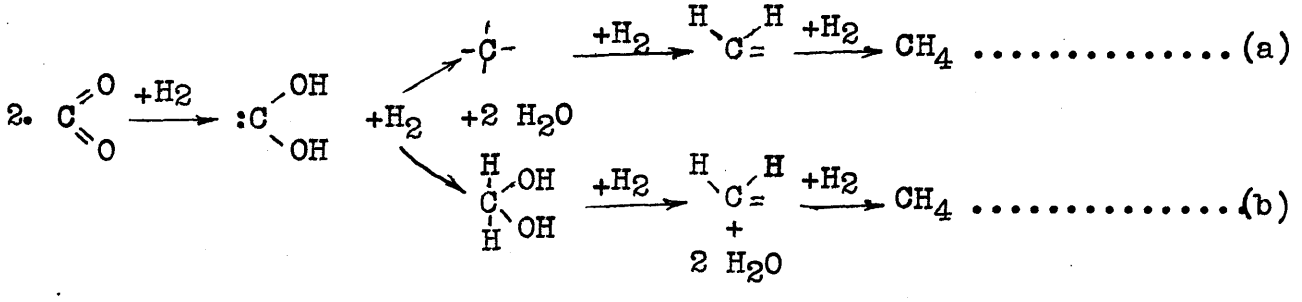
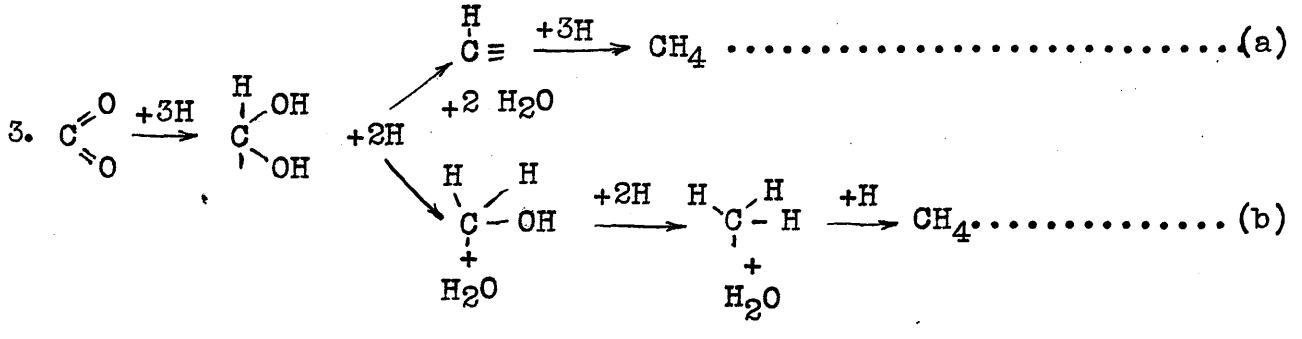
CHAPTER IV.

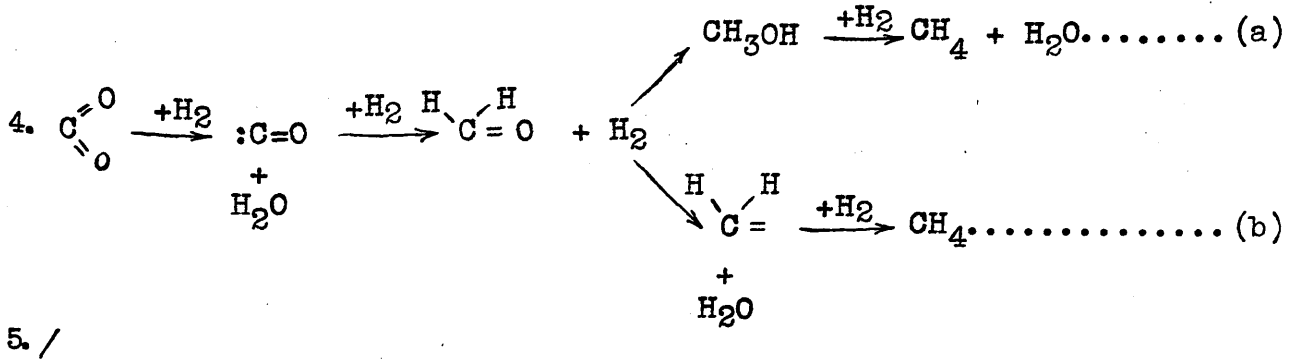
POSSIBLE MECHANISMS OF THE REDUCTION OF CARBON DIOXIDE TO METHANE.

From the discussions contained in the preceding chapters the following possible mechanisms for the reaction may be set down:-

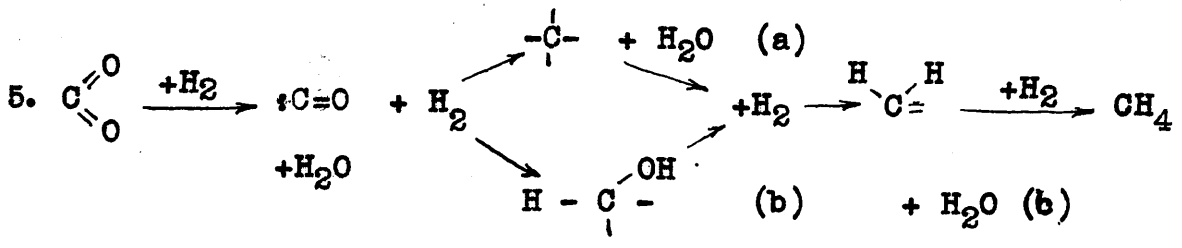




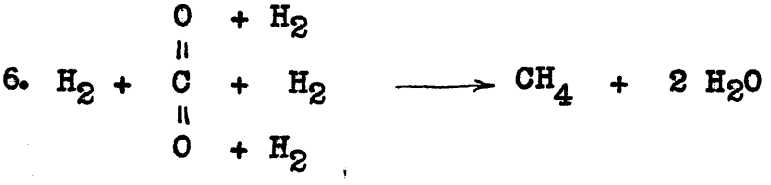




5. /

5. 

All the above mechanisms denote stepwise reduction of CO_2. It is also possible that four hydrogen molecules react simultaneously with a molecule of carbon dioxide:-

6. 

Mechanism 1(a) is that suggested by Pichler (73) and includes the possibility that the first step is either formic acid or dioxymethylene. In 1(b) the direct production of methylene radicals from formaldehyde without the intervening formation of methanol is postulated. It must be pointed out that in all the mechanisms listed above, the reacting hydrogen may be regarded as being in the atomic state irrespective of the symbols employed. Reaction 2(a) postulates the formation of "surface carbide" from dioxymethylene, while 2(b) considers the possibility of a complex $H_2\ C(OH)_2$ being formed as the next step, followed by removal of the two (OH) groups leaving a methylene radical.

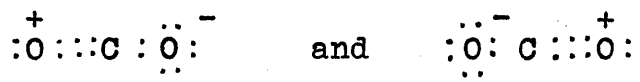
In/

In mechanism 3, it is assumed that when the two double bonds of the carbon dioxide molecule are broken either independently or by the interaction of hydrogen, one of the free bonds is utilised to anchor the compound to the catalyst surface, while all the other bonds are satisfied by the addition of three hydrogen atoms. The next step is the production of either a :CH or an $H_2 = \underset{|}{C} - OH$ radical. (3 b.) Instead of two hydrogen atoms acting on the primary radical and producing an $H_2 = \underset{|}{C} - OH$ radical, it is also possible that one hydrogen atom will act and produce an $H - \underset{||}{C} - OH$ radical instead. Wherever a :CH or a $:CH_2$ radical is postulated, the formation of a $\cdot CH_3$ radical is certainly possible before methane is produced.

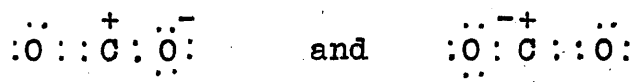
Mechanisms 4 and 5 postulate the primary production of carbon monoxide, in situ, on the catalyst surface. After that initial step reactions 4(a) and 4(b) are no different from 1(a) and 1(b). Mechanism 5(a) shows surface carbide as the next step, while 5(b) shows the possibility of an HCOH radical being formed as postulated by Zelinskii. (82)

In all the schemes shown above, the CO_2 molecule is pictured as if the oxygen atoms are at an angle to each other. That has been done merely for convenience. In reality the molecule is linear. (92) (93) The simple structure O = C = O is represented by $:\ddot{O}::C::\ddot{O}:$, where the double bond between/

between the oxygen and carbon atoms is made up by two electron pairs as shown. In addition to this simple structure resonance is supposed likely between the structures:



and the structures:



The C - O distance is given as 1.15 ± 0.02 Å. (93)

($\text{Å} = 10^{-8}$ cm.)

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CHAPTER V.

SOME KINETICAL CONSIDERATIONS.

Certain aspects of the kinetics of heterogeneous reactions need to be considered before proceeding on to the experimental section.

If a single reacting gas in equilibrium with a catalyst surface is considered, at equilibrium, the rates of condensation and evaporation of the gas molecules will be equal, so that we have the expression:-

$$(1 - \theta)\,\alpha\mu = \nu\theta$$

$$\text{or } \theta = \frac{\alpha\mu}{\alpha\mu + \nu} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where μ is the number of molecules, α is the fraction of molecules striking the surface which adhere, θ is the fraction of total surface covered with gas molecules at any instant, ν is a constant for the given gas and surface. In terms of pressure of the gas, the same can be expressed as:-

$$\theta = \frac{k_1 p}{k_2 + k_1 p}$$

where p is the pressure of the gas and k_2 and k_1 are constants.

In general, chemical reaction may be considered to occur between 'm' adjacent molecules, followed by immediate evaporation of the products; in the simplest case where 'm' is equal to unity we may finally arrive at the expression for the/

the rate of reaction to be:-

$$\frac{dx}{dt} = \frac{k_1 p}{k_2 p+1} \quad \ldots\ldots\ldots\

pressure and the process will be of a zero order. Examples of a nearly zero-order reaction are to be found in the catalytic decomposition of ammonia on the surface of tungsten (101) and the decomposition of hydrogen iodide on the surface of a heated gold wire. (102)

It is now seen that the two extreme cases are represented by expressions (3) and (4) and the general form for expression (2) would be:-

$$\frac{dx}{dt} = k\, p^{n} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where n lies between zero and one.

When the surface is almost completely covered, there is no distinction kinetically between processes which involve one molecule only of the reacting gas and those which involve two. Thus the changes $A \rightarrow B + C$ and $2A \rightarrow B + C$ would both be of zero order and indistinguishable.

Retardation by Reaction Products.

In some cases the products are capable of retarding the reaction by being strongly held on the surface. In the same way as before, we get the expression:

$$\frac{dx}{dt} = \frac{k_1\, p}{k_2\, p_1 + 1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

p being the pressure of the reactant and p_1 of the product; as the product accumulates it retards the reaction. If the reaction product is very strongly adsorbed on the surface we get:/

get:-

$$\frac{dx}{dt} = k \frac{p}{p_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

and the rate of reaction should be proportional to the pressure of the reactant, but inversely proportional to that of the product.

Two reacting gases.

When a reaction involves two or more gases, a number of possibilities may arise according as one or another, or neither of the reactants or products is strongly adsorbed. If in the first instance, a case is taken when the products are not adsorbed and the surface is sparsely covered by both reactants, and if the reaction is taken as:-

$$a\,A + b\,B \rightarrow \text{products}$$

we get the expression:

$$\frac{dx}{dt} = k_1 \, p_A^a \, p_B^b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

The order of the reaction should thus be a + b, in agreement with the number of molecules taking part.

If one of the reacting gases is firmly held, it may have the effect of retarding the reaction as its pressure is increased. If one molecule of A and one of B take part, A is strongly adsorbed and the fraction covered by B is negligible, the rate of reaction is given by:-

$$\frac{dx}{dt} = k_1 \, p\,B/p\,A \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

The/

The rate would then be inversely proportional to the pressure of the gas strongly held by the surface.

In the case where there is no inhibition by the reaction products, A adsorbed weakly and B somewhat more strongly:-

$$\frac{dx}{dt} = \frac{k\ pA\ pB}{(1 + bB\ pB)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

In this case the velocity goes through a maximum if pA is kept constant and pB varied, since B replaces A in the adsorption layer.

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EXPERIMENTAL SECTION.

PART I.

THE INTERACTION OF CARBON DIOXIDE AND HYDROGEN ON NICKEL CATALYSTS AT ATMOSPHERIC PRESSURE.

CHAPTER I.

PREPARATION OF CATALYSTS.

The nickel catalystsused in all the experimental work were supported on pumice. Pumice is a complex silicate of aluminium, sodium, potassium, calcium, magnesium and iron, and as a carrier in various grain sizes,has been used for many types of catalysts.

The pumice used in the preparation of the catalysts described here was found to contain considerable amounts of visible foreign matter. These were separated by washing the pumice in a wide basin under a flowing stream of water. The pumice particles being lighter, were carried away and collected in a basin beneath, leaving the heavier impurities behind. This method resulted also in the elimination of comparatively dense or abnormally large particles of pumice.

The pumice thus separated was repeatedly boiled with increasing concentrations of hydrochloric acid to remove all traces of iron and soluble material. The adhering acid was removed by repeated boiling with fresh quantities of water until the washings showed no further precipitate with silver nitrate. After a final wash with boiling distilled water, the pumice was dried thoroughly in a steam oven and stored for use.

Various methods of depositing nickel on pumice have been/

been suggested by different investigators. Brunel (103) impregnated granulated pumice in a thick paste of precipitated nickelous hydroxide. De Haen (104) used nickel formate and freshly precipitated nickel carbonate which were stirred into a paste with purified pumice. Medsforth (39) precipitated nickel by evaporating a solution of nickel nitrate with the pumice suspended in the solution.

This latter method was used for the catalysts described here. Nickel nitrate (C.P. grade) was used. A solution of the nitrate was made containing approximately 140 gms. per litre. This solution was analysed for its nickel content by precipitation with di-methyl glyoxime in the usual manner and found to contain 0.0259 gms/cc. of nickel. Since large quantities of catalysts were made, different solutions of nickel nitrate were made for the different batches described below and analysed as before. The above analysis refers to only one of these.

It was decided to use thorium oxide as the promotor and accordingly a solution was made using thorium nitrate (A.R. grade).

To the weighed quantity of pumice, appropriate volumes of the solution were added to provide the required weights of nickel and thoria in the reduced catalyst. The mixtures of pumice and solution were then evaporated gradually with stirring, the final evaporation being done on a water bath followed by drying in a steam oven. The nitrates thus deposited as evenly as possible on/

on the pumice, were ignited gradually in a muffle furnace to convert them to the oxides.

Catalyst IA.

Mesh size - 5-8. B. S. S., major portion in the region of 5 mesh.

Ni content- 10 per cent. on weight of pumice.

ThO_2 " - 3.06 per cent. on weight of pumice.

Ignited gradually for five hours. The final temperature was carried to 500°C., because the decomposition of thorium nitrate is considered to be complete at 500°C. (105)

Catalyst IB

Mesh size - 10-14 B. S. S.

Ni content - 10 per cent. on weight of pumice.

ThO_2 content- 3.1 per cent. on weight of pumice.

Ignited in same way as Catalyst IA.

Catalyst II.

Mesh size - 5-8 B. S. S.

Ni - 10 per cent. on weight of pumice.

Ignited gradually for two hours. Maximum temperature - 300°C.

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FIGURE 1 - REACTION UNIT.

REACTION UNIT.

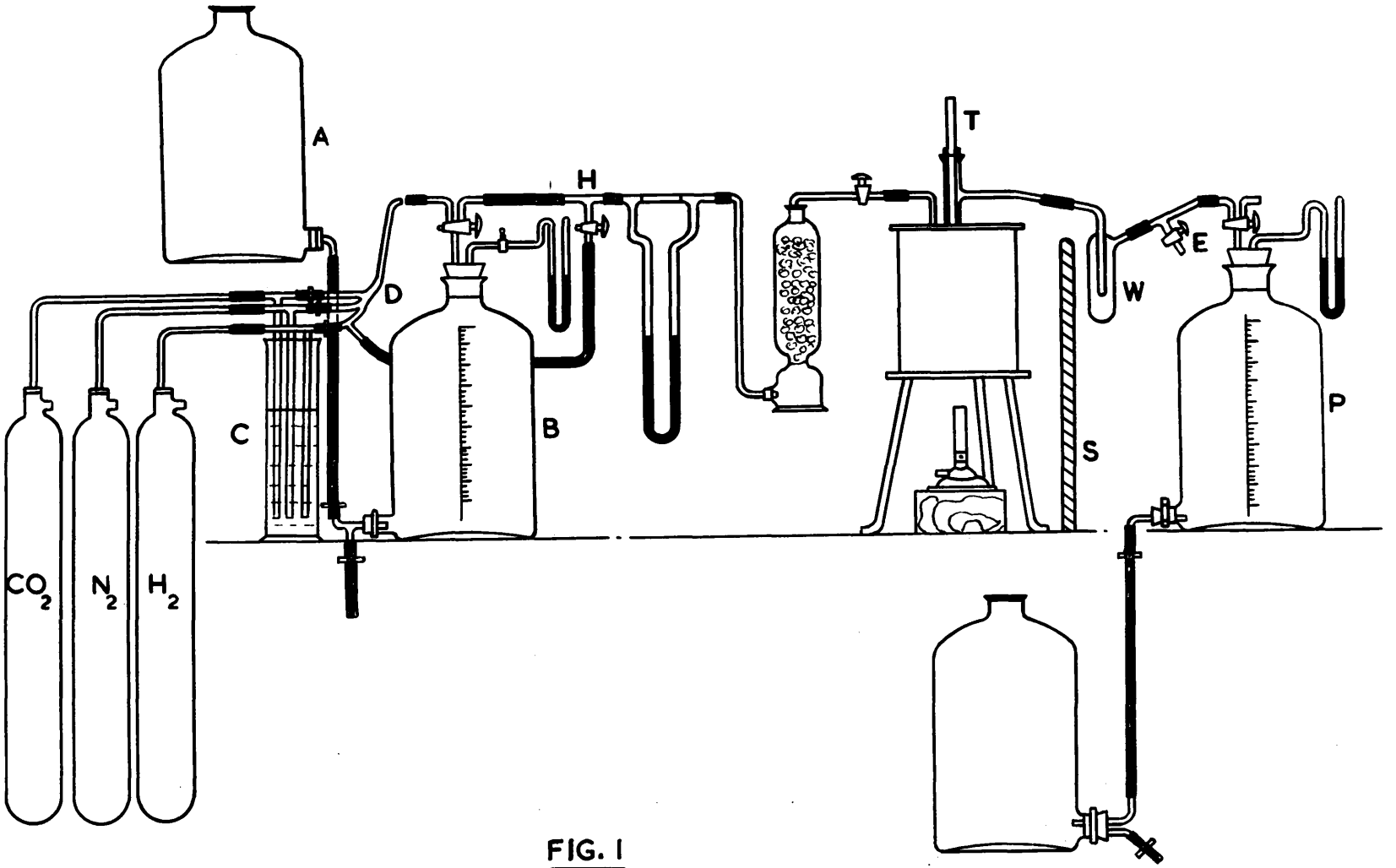

FIG. 1

CHAPTER II.

DESCRIPTION OF APPARATUS.

The reaction unit employed in its final form, consisted of the following as shown diagrammatically in Figure 1.

(i) A gas mixing and supplying unit consisting of two aspirators 'A' and 'B'. Aspirator 'B' was provided with a T-piece inlet tube at the bottom. The inflow and outflow of the confining liquid was regulated by means of screw-clips. The aspirator was graduated carefully and provided with a rubber bung carrying a mercury manometer and a two-way stop-cock. The gases employed were fed into this aspirator directly from the respective cylinders. The cylinder outlets were stoppered with ordinary rubber bungs and the gases fed on to the aspirator through leads provided with safety water-seal limbs, dipping in a glass cylinder 'C'. The three leads were provided with separate screw-clips and were connected to a common outlet 'D', which could be joined on to the stop-cock limb, as and when required. The lead from the hydrogen cylinder was provided with a side-tube which was connected directly through a stop-cock to the side-tube 'H' in the main system. This enabled hydrogen to be fed in directly into the system, thus by-passing the supply aspirator.

(ii) A flow-meter and a drying tower packed with calcium chloride/

chloride followed the above. Two flow-meters were prepared and calibrated with air to record rates of flow varying from 75-300 ccs./min. and from 300-1000 ccs./min. respectively.

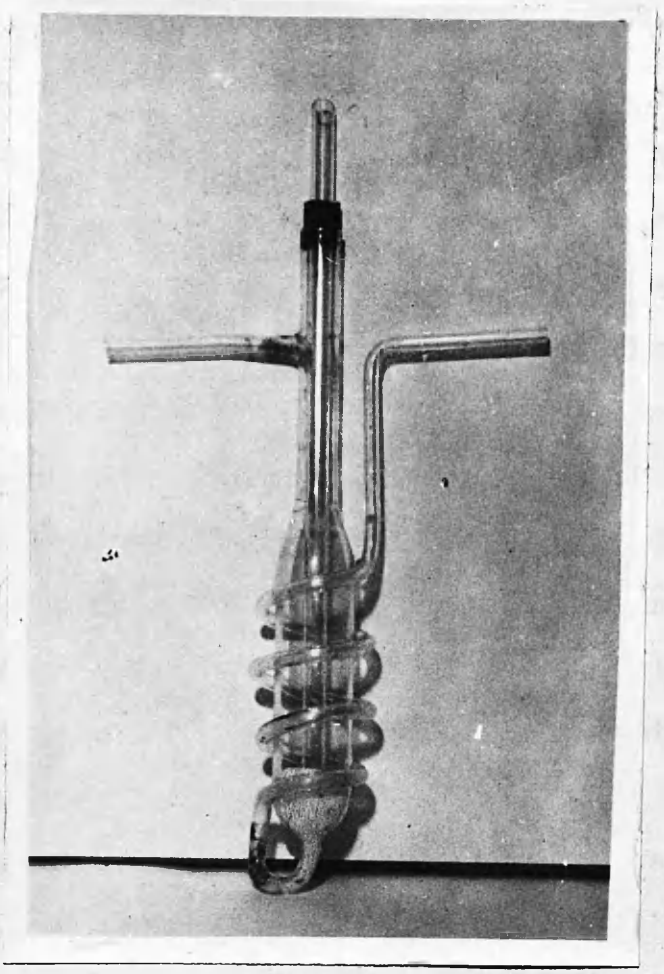

Figure 2. Reaction Chamber.

(iii) The reaction chamber (Figure 2) consisted of a pyrex tube widened at the bottom and provided with a side outlet at the top. The gases entered the chamber from the bottom through a coil wound round the chamber. The catalyst rested at the bottom of the tube supported by asbestos wool.

Into/

Into the catalyst mass was inserted a silica thermometer pocket 'T' carrying a thermometer recording up to 360°C. The entire reaction chamber was immersed in an oil bath lagged with asbestos and covered on top with asbestos board. The oil bath was heated by bunsen burners. A heavy oil with a fairly high boiling point was used. The entering gases were preheated as they passed through the coil surrounding the reaction chamber proper. The advantage of using an oil bath was that, having a large heat capacity, it was comparatively easy to maintain the temperature in the catalyst bed constant for long periods.

The asbestos wool employed in supporting the catalyst mass was found to contain appreciable amounts of alkali; the wool was therefore boiled with dilute hydrochloric acid, washed free of acid and dried. Small quantities were ignited thoroughly before use.

(iv) The outlet of the reaction chamber was connected through a trap 'W' to the receiving aspirator 'P'. A side tube 'E' was connected in between. The aspirator 'P' was also graduated and provided with a two-way Stop-cock and manometer. An asbestos shield 'S' was placed between the oil bath and the collecting aspirator in order to prevent radiation of heat to it.

Saturated brine containing 1 per cent. sulphuric acid was used as the confining liquid.

Experimental/

Experimental Procedure.

A small amount of alkali-free ignited asbestos wool was introduced into the clean dry catalyst chamber and levelled. A definite volume of catalyst was weighed in a stoppered weighing bottle. The same volume was obtained each time by filling the weighing bottle up to a certain mark on the bottle by gentle tapping. Obviously, in view of the heterogeneity of the catalyst, it was impossible to ensure that exactly the same volume had been taken each time. The volume thus measured was the total space occupied by the catalyst resting by natural packing and including the voids.

A comparison of the weights of different batches of catalyst measured in this way, however, showed that reasonable agreement could be obtained each time. ($\pm$ 2 per cent).

The weighed catalyst was then transferred carefully on to the asbestos support in the reaction chamber, the thermometer pocket was introduced and the catalyst mass evenly distributed round the end of the pocket by means of tapping. Care was taken to insert the pocket to such an extent as to ensure that the thermometer bulb lay about midway in the catalyst mass. The reaction chamber was then connected on to the system; the air in the system was flushed out by means of hydrogen through the side tubes provided and the oil bath was gradually heated up. The average temperature of reduction was about 290°C., but it often/

often rose to 320°C. for short periods. The reduction was carried out for about 12 hours in a slow stream of hydrogen. (About 2.0 litres per hour). Subsequent to reduction, the catalyst was always kept in an atmosphere of hydrogen and never exposed to air.

Before each run a synthesis gas mixture was prepared in the supply aspirator. In each case the lighter gas, hydrogen, was introduced first after ensuring that all residual gases had been flushed out from the tubes leading up to the aspirator. The heavier gases, nitrogen and carbon dioxide, were then introduced as required. Hydrogen and nitrogen were taken directly from large industrial cylinders and no efforts made to purify them. The carbon dioxide was taken from a small cylinder intended for medical use and was found to contain only traces of impurities.

The suppliers of the hydrogen cylinder (British Oxygen Co.) gave the following estimate of the impurities present in the hydrogen:-

CO	-	8.4 - 16 volumes/million.
CO_2	-	3 - 22 volumes/million.

Other Carbon compounds

as CO_2	-	19 - 58 volumes/million.
O_2	-	0.005 - 0.2 per cent.
N_2	-	0.04 - 0.75 per cent.

NH_3/

NH_3 - 0.16 - 4.5 volumes/million.

Hg - 1×10^{-5} gms./ft.^{3}

SO_2 and SO_3 - Absent.

It will be observed that the only appreciable impurities are oxygen and nitrogen, which together vary within the limits 0.045 - 0.95 per cent.

The nitrogen used contained about 0.2 per cent. of oxygen.

After filling up the supply aspirator, the gas mixtures were allowed to stand for about an hour, with occasional shaking to ensure uniform mixing. Because of the high solubility of carbon dioxide, it was found necessary to sample and analyse the gas mixtures immediately before a run was commenced. Similarly, the product gases were also analysed as soon as possible after the end of each run. As far as possible, the confining fluid was saturated with a gas of the same composition as that used in the reaction.

Before commencing a run, the reduced catalyst was heated up gradually to the required temperature in an atmosphere of hydrogen. The temperature was then maintained slightly below that required for the run, the hydrogen supply was cut off, and the synthesis gas mixture was allowed to flow through the system and out through the end side tube at the same rate at which the actual run was to be operated. Since the reaction is/

is highly exothermic, this initial passage of synthesis gas helped to bring the temperature to a steady mark. About two litres of synthesis gas was used in this way before each run. Immediately after this initial passage, the gas volume in the supply aspirator was recorded, the side outlet was closed, the collecting aspirator connected and the run commenced. By operating screw-clips connected to both aspirators the flow was adjusted to the required rate. During a run the entire system was kept at a positive pressure of about 1 cm. of Hg. Since the flow-meter had been calibrated with air, for varying compositions of carbon dioxide, hydrogen and nitrogen, the actual rate of flow varied for the same amount of indication on the flow-meter. It was therefore decided to use the flow-meter only as an approximate indicator. The actual rate of flow of the inflowing gas was obtained by timing the run accurately with a stop-watch and by noting the exact volume passed during the run. Care was taken to ensure a steady rate of flow throughout each run; in the case of runs of short duration, the rate of flow as recorded is really the average.

Immediately after a run the system was purged of residual reaction gases. The catalyst chamber was allowed to cool in an atmosphere of hydrogen and thus maintained until the next run.

The volume of the product gas was measured as accurately as/

as possible and the temperature and barometric pressure noted. The gas was then sampled and analysed without delay.

All analyses were carried out in a "Macfarlane" Gas Analysis Unit. (106) This type of unit is a modification of the Hempel. It has several advantages over the ordinary Hempel unit:-

(a) The gases are measured and also exploded over mercury.

(b) Constant temperature for measurement of volumes is assured by a water jacket.

(c) The absorption pipettes, being detachable, can be vigorously shaken, ensuring complete removal of the smallest traces of the component.

(d) A complete analysis can be performed in about thirty minutes.

One disadvantage is that the volume of gas taken for analysis is 50 ccs. instead of 100. The volume is, however, easily read to 0.05 ccs. and this limit of accuracy is usually sufficient.

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CHAPTER III.

EXPERIMENTAL DATA AND DISCUSSION.

The first few runs were exploratory in nature and were carried out in order to determine the experimental conditions and catalyst activity. In the succeeding tables results commencing from Experiment No. 4 have been tabulated. The following is a sample calculation:-

Experiment No. 4.

Synthesis Gas Composition. per cent.		Product Gas Composition. per cent.
CO_2	14.8	3.8
O_2	0.5	0.3
CO	-	0.6
CH_4	-	28.0
H_2	84.5	67.0
N_2	0.2	0.3

Volume of Gas passed - 4100 ccs.

Volume of Gas collected - 1920 ccs.

Time of run - 31 mins.

Rate of flow - 132 ccs./min.

Temperature - 280°C.

Catalyst - Ni-ThO_2 - pumice - IA.

Volume of catalyst (with voids) = 18.0 ccs.

Weight of catalyst (unreduced) = 11.06 gms.

CO_2 Balance:- Amount CO_2 Passed = 607 ccs.

Amount CO_2 Recovered:-

as CO_2 = 72.9 ccs.

as CH_4 = 537.5 ccs.

610.4 ccs.

TABLE I.

Catalyst I A..... 10% Ni and 3% ThO_2

Volume of Catalyst = 18.0 c.cs.

Weight of Catalyst = 11.07 gms.

TABLE I,

Expt. No.	Time of run. mins.	Synthesis Gas %			Product Gas %					Temp °C.	Rate C.cs/ min.	C.cs CO_2 convt. /cc.cat/ min.
		CO_2	H_2	O_2	CO_2	H_2	CH_4	O_2	CO			
4	31	14.8	84.5	0.5	3.8	67	28.0	0.3	0.6	278.0	132	0.96
5	13	14.5	84.6	0.2	5.3	76.4	17.9	0.0	0.1	275-8	308	1.91
6	7.5	14.7	84.6	0.2	11.3	78.1	8.9	0.3	0.1	275	546	2.14
7	10	14.4	84.3	0.4	8.3	76.3	13.0	0.0	0.5	275-8	400	1.95
8	10	14.8	84.6	0.4	10.1	77.1	11.0	0.2	0.2	278	400	1.73
9	29	14.0	84.2	0.6	5.3	72.4	20.0	0.2	0.4	275-8	138	0.87
10	29	14.0	85.0	0.4	6.2	74.7	17.8	0.0	0.2	275-8	136	0.82

Yield:- ccs. CO_2 converted/cc. of cat./min.
or
ccs. CH_4 formed/cc. of cat./min.

$$\text{i.e.} \quad \frac{537.5}{18.0 \times 31} = 0.962$$

No estimation of CO was made in the initial gas. The figures for CO in the product gas, as is shown in Table I, are very small and range from 0.1 to 0.6 per cent. These figures are not likely to be accurate in all cases because small quantities of CO are always difficult to estimate. Apart from the accuracy of volume measurement in the apparatus employed, the figure varies with the freshness and purity of the absorption solutions employed in the analysis. In view of the very small quantities detected in the products, the estimation of CO was given up in later experiments. The significance of the presence of CO will be discussed later on.

It will be noted that small quantities of oxygen were always detected and estimated. The oxygen could have arisen either from the gases employed, or from dissolved air in the brine used, or through slight leaks and air pockets encountered while transferring the gases to the aspirator. Oxygen has been found in most cases both in the initial as well as in the product gases.

The temperature, as has been pointed out earlier, was difficult to control. The values in the tables are all really averages/

averages of the slight fluctuations noted. In such highly exothermic reactions the actual temperature of the surface of the catalyst can hardly be determined. In spite of the precaution taken of passing a certain amount of gas through the catalyst before starting the run, it was very difficult to attain the same temperature each time. The quantities of heat generated depended on the extent of the conversion, and the temperature recorded was also dependent on the rate at which heat was dissipated.

The maintenance of absolutely constant temperature throughout all experiments can only be accomplished by the use of very large quantities of synthesis gas - thus allowing sufficient time for temperature adjustment. In the experiments, however, the temperature fluctuations were not large. ($\pm$ 2.5°C.)

The catalyst composition, as has been pointed out, is stated on the fully reduced basis. No attempt was however made to carry the reduction to completion. It was considered sufficient to reduce it to the same extent each time. Small variations in conditions are not likely to have a large effect, especially when the reduction is carried out over a period of 12 - 14 hours. Then again, if Ipatieff's statement (53) that nickel and nickel oxide are equally effective in this reaction is correct, the effect of small differences in reduction should be nil or negligible.

Effect/

Effect of Rate of Flow.

In practice, the capacity of a given system is expressed in terms of space velocity, i.e. volume of gas passed/vol. of catalyst/unit time. In any system as the space velocity is increased from zero, the conversion, starting from equilibrium value, falls off until, the velocity reaching a very high value, the conversion, due to decreased time of contact is very small. At the same time, however, the yield per unit time rises from a low value, passes through a maximum and then decreases. If, as the velocity is increased, the conversion is not markedly affected at first, a condition frequently met with, the yield rises in proportion to the amount of material treated per unit of time. Then unless the reaction rate is very rapid, the conversion may decrease, with increasing velocity, faster than is proportional to space velocity increase. In such cases, the yield per unit time begins to decrease. But before this falling off starts, the maximum in the yield curve should be followed by a portion indicating constant yield.

In all the experiments described here, the rate of reaction is the yield of final product in unit time, i.e. ccs. of CO_2 converted or ccs. of CH_4 formed/cc. of catalyst/minute.

Graphs 1 and 2 corresponding to Tables I and II of this series of experiments show that the rate of reaction in most/

TABLE II.

TABLE II

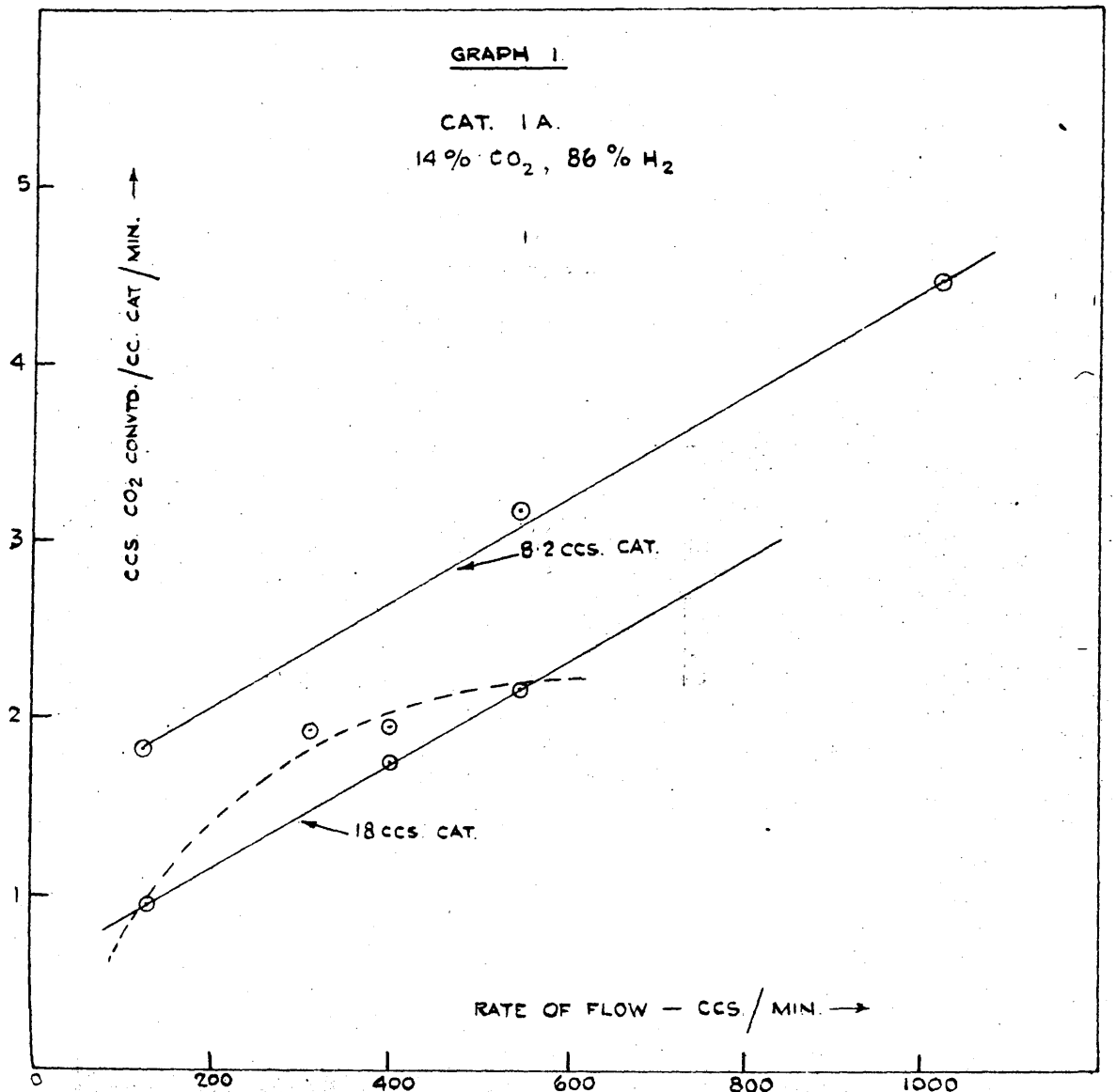
Catalyst I A.....10% Ni and 3% ThO_2. Volume of Catalyst.....8.2 c.cs.

Expt. No.	Time of run. mins.	Synthesis Gas %			Product Gas %				Weight of Catalyst gms.	Temp. °C.	V Rate cc./ min.	C.cs CO_2 convtd./ c.c.cat/ min.
		CO_2	H_2	O_2	CO_2	H_2	CH_4	O_2				
11	32	14.2	85.0	0.1	4.6	73.5	21.4	0.1	5.32	280	125	1.82
12	7.5	14.4	85.0	0.3	11.7	79.8	5.6	0.2	5.32	275-8	546	3.19
14	3.75	13.6	86.0	0.2	12.3	74.8	5.9	0.5	5.19	289	1118	5.98
15	4.0	14.1	85.0	0.2	12.0	82.0	3.9	0.4	5.19	275	1025	4.46
16	4.75	18.3	80.8	0.5	17.5	73.1	4.1	0.1	5.26	280	910	4.03
17	8.5	17.0	82.0	0.4	15.9	73.2	4.9	0.4	5.26	275-9	470	2.35
18	6.0	19.2	80.0	0.5	17.0	76.8	4.2	0.2	5.22	275-8	683	3.14
19	6.0	24.7	74.0	0.5	24.6	67.5	3.6	0.3	5.22	275	666	2.46
20	9.5	24.0	73.0	0.2	26.5	65.6	6.6	0.2	5.20	278	422	2.25
21	5.0	25.4	73.5	0.4	25.3	65.2	3.0	0.2	5.20	278	800	2.73
22	10.0	49.0	49.0	0.3	54.0	41.0	3.4	0.7	5.20	275	400	1.31
23	7.75	49.6	49.6	0.2	55.5	39.0	4.7	0.3	5.30	275	516	2.17
24	5.75	48.9	50.0	0.3	51.4	40.3	4.9	0.2	5.30	280	695	3.56

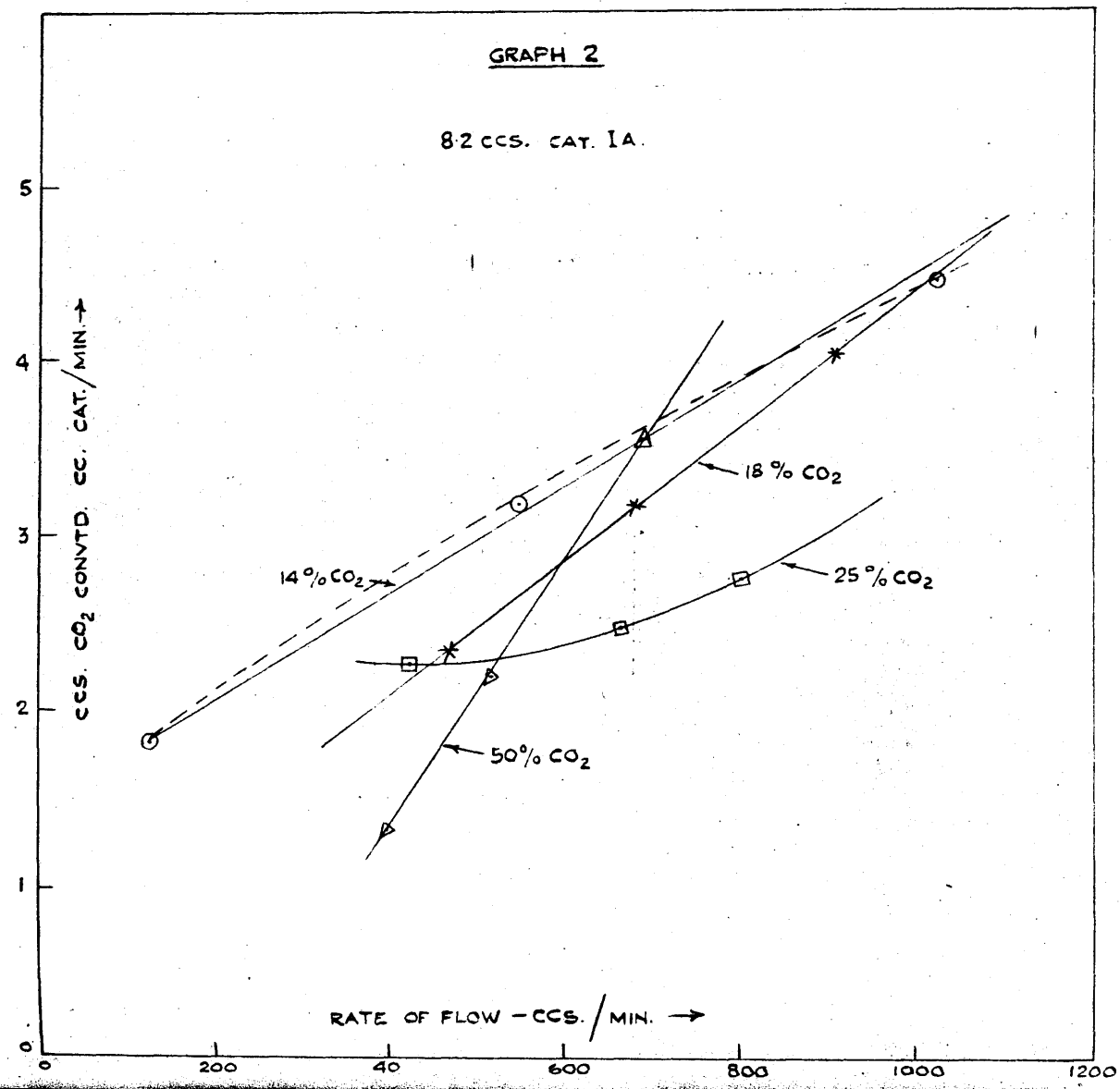
TABLE II A.

Expt. No.	Carbon dioxide Balance.				
	In Gas Collected.			In Gas Passed c.cs.	Recovery %
	As CH_4 c.cs.	As CO_2 c.cs.	Total c.cs.		
11	470	101	571	568	100
12	196	409	605	590	98
14	184	384	568	568	100
15	146	444	590	578	102
16	157	671	828	788	105
17	164	534	698	679	102
18	155	626	781	787	99
19	121	835	956	987	97
20	176	703	879	960	92
21	112	945	1057	1017	104
22	108	1720	1828	1960	93
24	168	1763	1931	1955	99

GRAPH 1.


GRAPH 1.
CAT. 1 A.
14 % CO_2, 86 % H_2
CCS. CO_2 CONVTD. / CC. CAT / MIN. →
8·2 CCS. CAT.
18 CCS. CAT.
RATE OF FLOW — CCS / MIN. →
0
200
400
600
800
1000
1
2
3
4
5

GRAPH 2.


GRAPH 2
8·2 CCS. CAT. IA.
CCS. CO_2 CONVTD. CC. CAT./MIN.
RATE OF FLOW – CCS./MIN.
14 % CO_2
18 % CO_2
25 % CO_2
50% CO_2
0
1
2
3
4
5
200
40
600
800
1000
1200

most cases increased linearly with increasing rate of flow, within the range studied. The results seemed to suggest that the reaction rate is governed by diffusion of the reactants through a film of relatively stagnant gas on the catalyst surface and the rate of reaction therefore appeared to be proportional to some power of the gas velocity. From theories on heat transfer, it is known that with forced flow of gases or water, the flow being turbulent in character, the film-transfer coefficient can be greatly increased by increasing the velocity of flow of the fluid. For the case of turbulent flow of gases inside clean tubes, the film coefficient is considered proportional to some form of velocity figure raised to the power 0.8.

Again, the flow characteristics through a catalyst bed might be considered to more nearly resemble gas flow normal to a bank of staggered tubes. The film transfer coefficient in such cases is considered to be proportional to $V^{2/3}$ or $V^{0.66}$ (107), where V is the linear velocity.

The actual velocity of flow through a catalyst bed is difficult to estimate, since it is dependent on the passage available between the catalyst particles, which again is a function of the size distribution, shape and nature of packing of the catalyst particles. It can, however, be reasonably assumed that for each catalyst batch the latter factors are the/

the same in each case; the linear velocity through the bed is then obtained as a function of the volume of flow per unit time.

Graph 1 shows that for 8.2 cc. of catalyst, when the yield is plotted against velocity of flow, a straight line is obtained. Similar relationships for varying concentrations of reactants, are shown in Graph 2. The curve for 25 per cent. CO_2 - 75 per cent. H_2 is peculiar in comparison to the others. The slopes of the graphs are also shown to be varying in relation to each other. When the same graphs were plotted on a log-log graph paper, the following values of the slope were obtained:-

14 per cent. CO_2..... Slope - 0.418

18 per cent. CO_2..... Slope - 0.716

50 per cent. CO_2..... Slope - 1.75

If the slopes were of the order of 0.7 - 0.8 and if the slopes for all the graphs were the same, then there would have been justification for considering diffusion through a gas film as the controlling factor.

The results can, however, be examined in a different way. Instead of plotting the reaction rates against simple velocity of flow, they may be plotted against the Reynolds Number, $Re = \frac{DV\rho}{\mu}$. D will be constant for all experiments - but V, ρ and μ will be varying. In actual practice, the Reynolds number is calculated by expressing each factor in certain/

certain conventional units. In this particular case, however, comparative rather than absolute values of this number were desired, and the units were therefore chosen arbitrarily. The numbers thus obtained can be termed as f(Re).

V was expressed as rate of flow in ccs./min.

ρ, or the average density of the gas mixtures was calculated from the percentage composition and the respective gas densities. These density values were taken from the International Critical tables and are for 0°C. No attempt was made to correct them to the reaction temperature because the temperature coefficients of the individual gases do not vary much in relation to each other. The values for ρ were:-

H_2 - 0.8987×10^{-4} gms./cc.

CO_2 - 19.7600×10^{-4} gms./cc.

The viscosity μ, of each gas was also taken from the Critical tables and the nett viscosity calculated from the composition of each gas mixture. In this case, however, the viscosity values had to be corrected to 285°C * or 558° K, by using the Sutherland relationship,

$$\eta = \eta_o \frac{T_o + C}{T + C} \left(\frac{T}{T_o} \right)^{3/2} \text{(C = Sutherland's constant).}$$

The value of C varies for each gas, thus C (H_2) = 72, and C (CO_2) = 274.

η_o at the corresponding temperature T_o was obtained from/

* (About 5° higher than recorded temperatures).

from the critical tables.

Thus for hydrogen,

$$\eta_{558} = 88.7 \times \frac{293 + 72}{558 + 72} \left(\frac{558}{293}\right)^{3/2} \times 10^{-6} \text{ poises}$$

$$= 135 \times 10^{-6} \text{ poises.}$$

Similarly, for carbon dioxide,

$$\eta_{558} = 260.8 \times 10^{-6} \text{ poises.}$$

In this way, $f(\rho)$, $f(\mu)$, $f(\frac{\rho}{\mu})$ and $f(Re)$ for each experiment have been calculated and recorded in Table III.

TABLE III/

TABLE III.

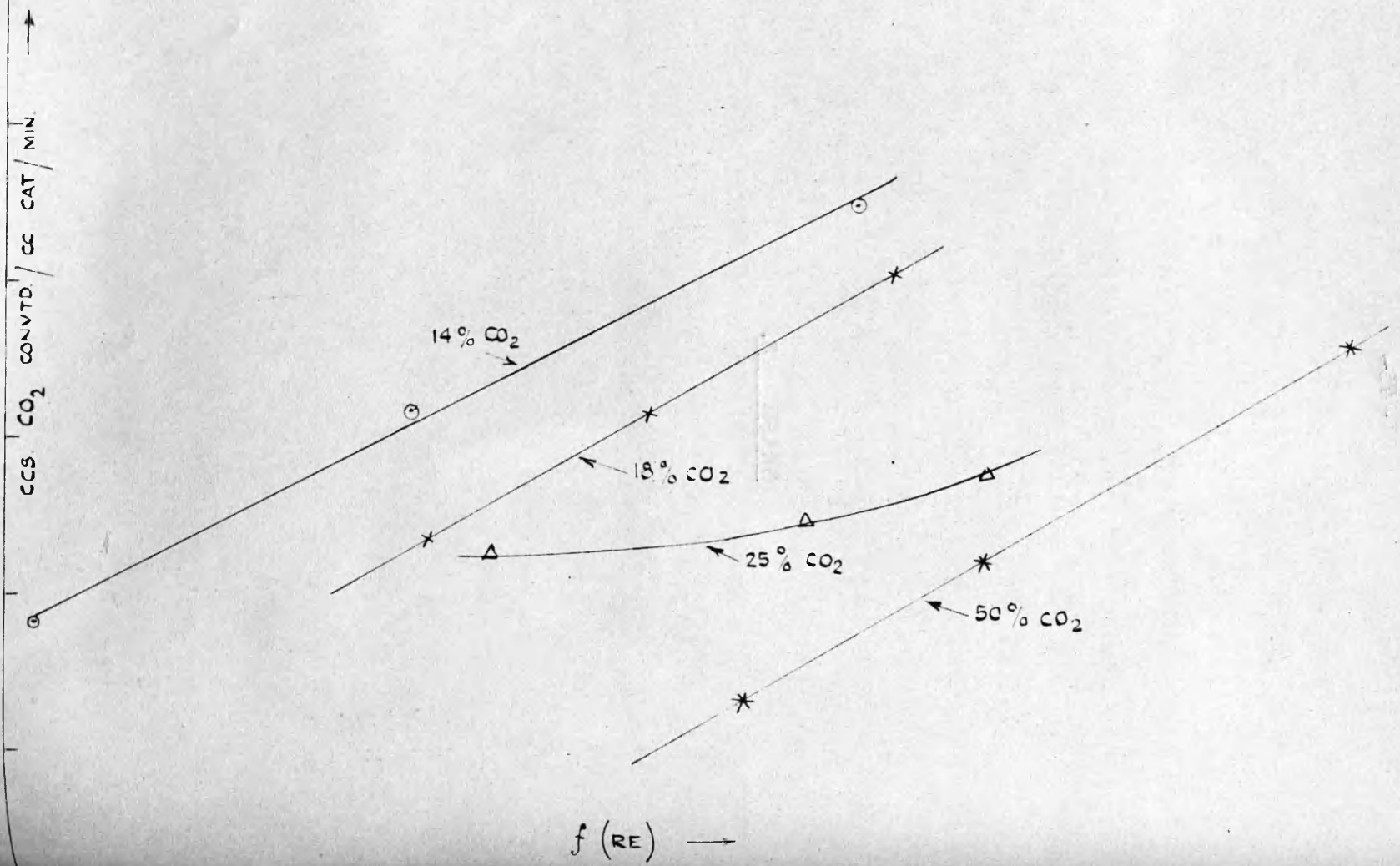
Expt. No.	% CO_2	% H_2	f(ρ) mixt.	f(μ) mixt.	f $(\frac{\rho}{\mu})$ mixt.	f(V)	f(Re)	Yield.
11	14	86	3.54	152.5	2.33	12.5	29.1	1.82
12	14	86	3.54	152.5	2.33	54.6	127.2	3.19
15	14	86	3.54	152.5	2.33	102.5	238.5	4.46
16	18	81	4.29	157.4	2.72	91.0	247.0	4.03
17	18	81	4.29	157.4	2.72	47.0	128.0	2.35
18	18	81	4.29	157.4	2.72	68.3	185.5	3.14
19	25	74	5.62	166.0	3.38	66.6	225.5	2.46
20	25	74	5.62	166.0	3.38	42.2	143.0	2.25
21	25	74	5.62	166.0	3.38	80.0	270.0	2.73
22	50	50	10.32	198.0	5.22	40.0	209.0	1.31
23	50	50	10.32	198.0	5.22	51.6	270.0	2.17
24	50	50	10.32	198.0	5.22	69.5	363.0	3.56

Common/

GRAPH 3.

GRAPH 3

8·2 CCS. CAT. I A



Common factors like 10^{-6}, 10^{-4} etc. were omitted wherever necessary and comparative values of f (Re) thus obtained. Graph 3 shows the results obtained when the yield per unit time was plotted against f(Re). The graphs for 14 per cent. CO_2, 18 per cent. CO_2 and 50 per cent. CO_2 run almost parallel to each other, and the 25 per cent. CO_2 results show some abnormality. When plotted on a log - log graph paper as shown in Graph 4, the slopes are:-

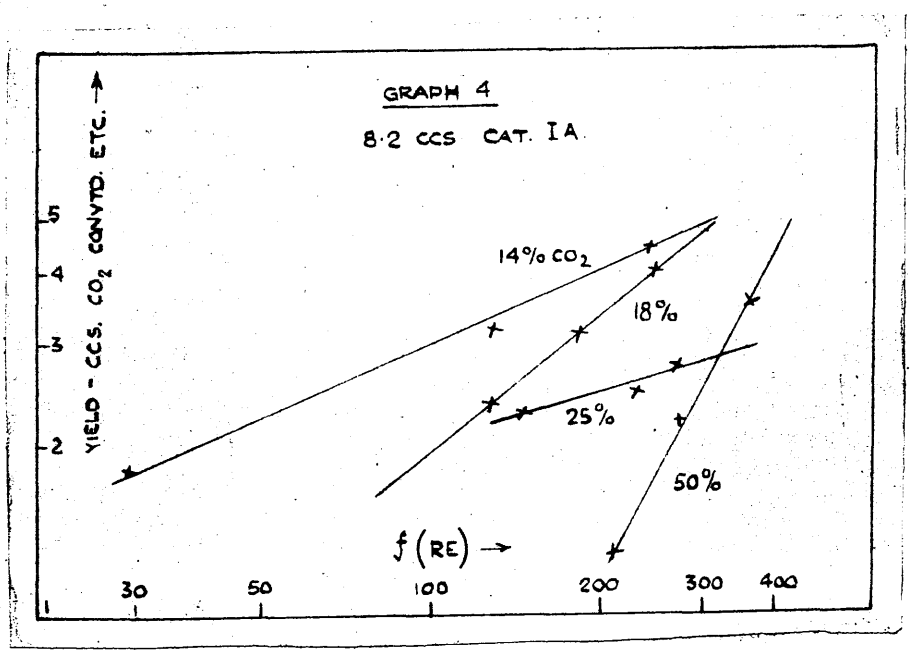
for 14 per cent. CO_2 .....0.427

18 per cent. CO_2 .....0.80

25 per cent. CO_2 .....0.29

50 per cent. CO_2 .....1.87

There is thus no very definite correlation between yield and f (Re).



Effect of Simultaneous variation in the concentration of both reactants.

Before considering the effect of simultaneous variation of the concentration of the reactants, it is to be noted from Table I that the reaction rate under identical conditions, gradually diminished as the number of runs on the same catalyst mass were increased (cf. Expts. 4, 9 and 10, and Expts. 7 and 8). This indicated that the catalyst mass was gradually losing activity. Impurities in the gases could have been responsible for this poisoning, but the more likely cause would be the deposition of carbon on the catalyst surface. Such a possibility has been shown by Randall and Schiffler. (56). Another cause could have been the presence of impurities in the asbestos packing on which the catalyst rested. Untreated asbestos wool was used in the experiments recorded in Table I. Tests showed that the asbestos contained traces of alkali. In subsequent experiments the asbestos wool was treated with acid, washed and ignited before use. Nevertheless, in order to avoid the effect of gradual loss in activity, experiments commencing from Table II were conducted on freshly reduced catalyst with about 3 - 5 runs per batch. It was also decided to use a smaller quantity of catalyst amounting to about 8.2 ccs. (with voids), commencing from Table II.

It will be noticed from Graph 1 that the yield per c.c. of catalyst is greater with 8.2 ccs. of catalyst than with

18/

18 ccs. This may mean that the end layers of catalyst when using a larger volume and when CO_2 concentrations fall rapidly due to conversion, become relatively ineffective, or rather less effective in conversion. Certainly the ideal arrangement would be to use just a thin layer of catalyst, but that is accompanied by several difficulties in experimentation.

Graph 2 (corresponding to Table II) shows the results when the concentrations of carbon dioxide were varied with corresponding variation in the concentration of hydrogen. The graphs intercross and the curve for 25 per cent. CO_2 is peculiar in comparison to the others. In Graph 3 the introduction of f(Re) clarifies the position. The lines of reaction rate draw apart as the possible effect of a gas film is taken into account. There appears to be no doubt that for equal values of f(Re), the reaction rate is diminished as the CO_2 concentration is increased.

Graph 2 may be considered in another way. If the simplest case, when one reactant 'A' is strongly adsorbed, is considered, then

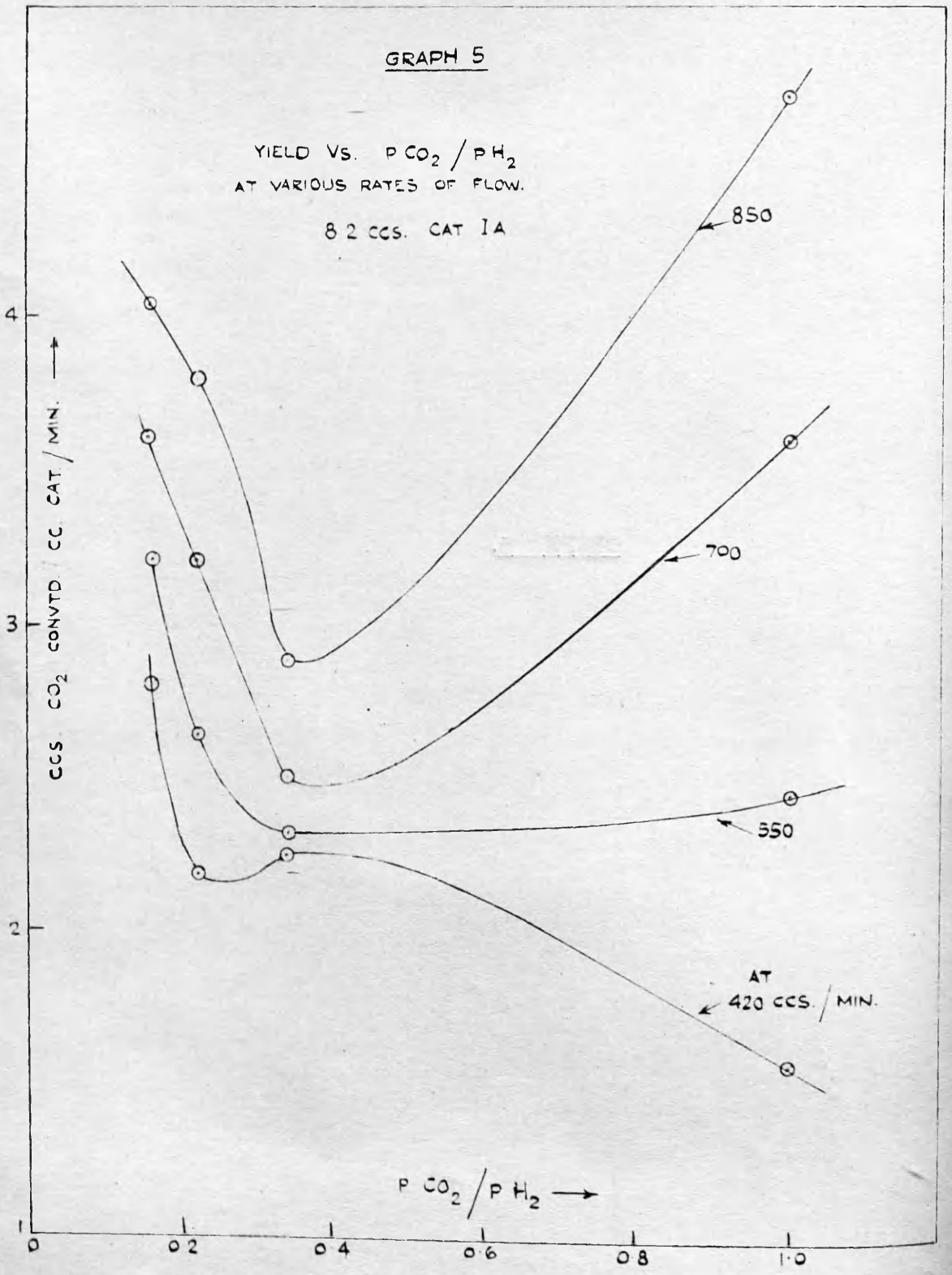
$$dx/dt = k.p\ B/p\ A.$$

If it is assumed that hydrogen is strongly adsorbed, as is likely with nickel catalysts, then the simplest relation would be

$$dx/dt = k.p\ CO_2/p\ H_2$$

Table IV gives the yields at various rates of flow for different values of the ratios of the partial pressures of the

GRAPH 5.


GRAPH 5
YIELD VS. P CO2 / P H2
AT VARIOUS RATES OF FLOW.
8 2 CCS. CAT IA
850
700
550
AT
420 CCS. / MIN.
CCS. CO2 CONVTD / CC. CAT / MIN.
P CO2 / P H2
4
3
2
1
0
0 2
0 4
0·6
0 8
1·0

GRAPH 6.

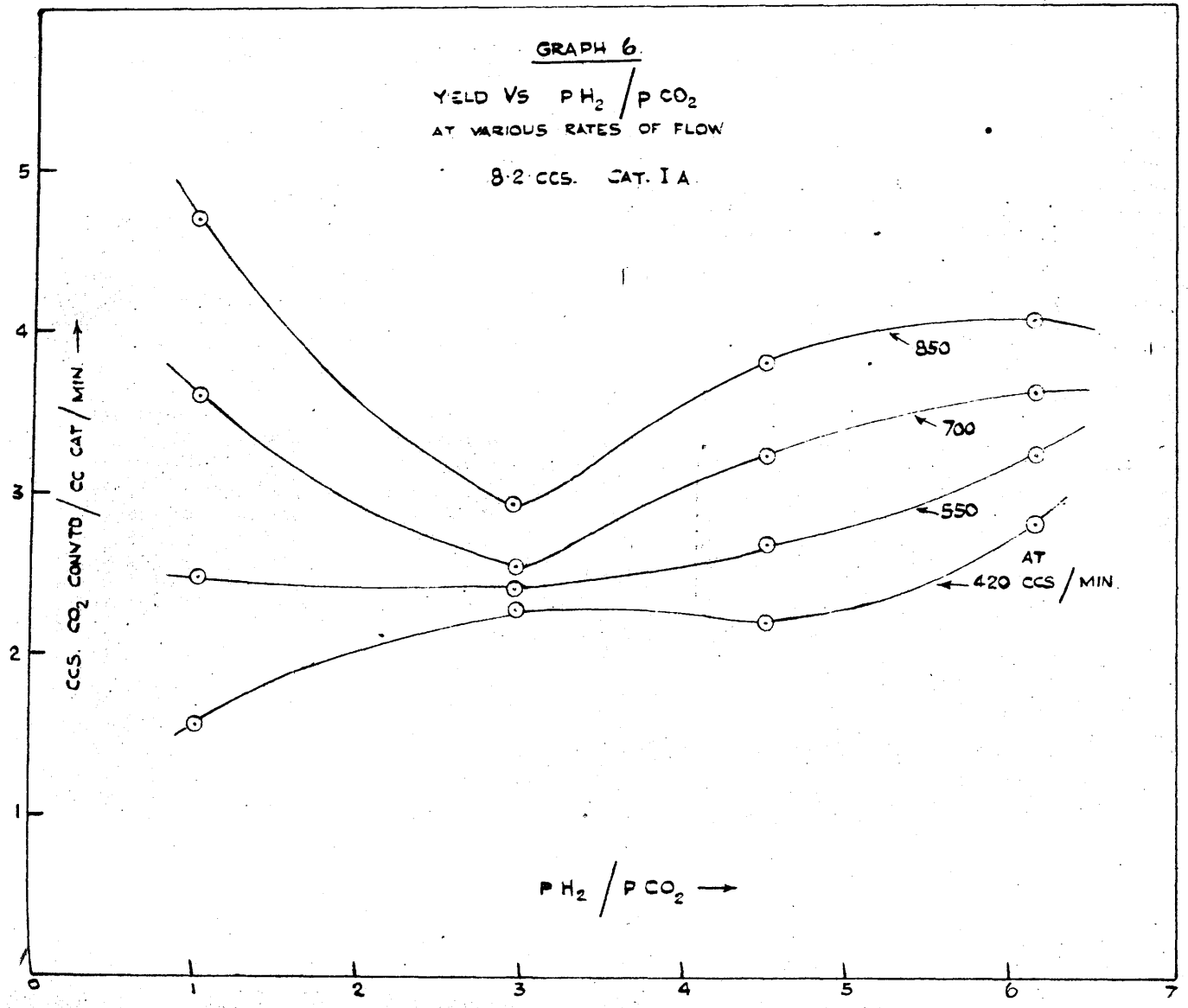

GRAPH 6.
YIELD VS P H2 / P CO2
AT VARIOUS RATES OF FLOW
8·2 CCS. CAT. I A
CCS. CO2 CONVTD / CC CAT / MIN.
P H2 / P CO2
850
700
550
AT
420 CCS / MIN.
0
1
2
3
4
5
6
7

TABLE IV.

Expt. Nos.	pCO_2	pH_2	pCO_2/pH_2	pH_2/pCO_2	Yield per unit time at V(ccs./min). = 420	550	700	850
11-15	0.14	0.86	0.16	6.14	2.8	3.20	3.60	4.04
16-18	0.18	0.81	0.22	4.50	2.18	2.64	3.20	3.80
19-21	0.25	0.74	0.34	2.96	2.25	2.32	2.50	2.88
22-24	0.49	0.49	1.00	1.00	1.57	2.45	3.60	4.70

Graph 5 shows several peculiar features. At a low gas velocity (420 ccs./min.), the reaction rate falls as pCO_2/pH_2 is increased. At higher velocities, there is a rise when $pCO_2/pH_2 = 1$. The curves in general seem to indicate that it is rather CO_2 which is strongly adsorbed. This is shown in the corresponding graph for pH_2/pCO_2 (Graph 6) where there is an initial fall as pH_2/pCO_2 is increased, only at high velocities.

Considering the case when the products are not adsorbed, and the surface is sparsely covered by both reactants, the expression is:-

$$dx/dt = k.p_A^a \; p_B^b$$

or/

or in this case, $dx/dt = k.(pCO_2)\ (pH_2)^4$.

Applying this expression in the same way, anomalous curves were again obtained. These curves have not been included. Such simple relationships, therefore, do not explain the results.

The overall conclusion, however, seems to be that both reactants are being adsorbed on the catalyst and that Carbon dioxide appears to be more strongly adsorbed.

Effect of varying the partial pressure of one reactant.

Under atmospheric pressure it is not possible to vary the partial pressure of one reactant while keeping that of the other constant, without the introduction of a third gas to make up the difference. Accordingly, nitrogen was used in this way in the series of experiments described here. The effect of nitrogen on a nickel catalyst at temperatures near 300°C. is held to be negligible.

The experiments are recorded in Tables V and VI, but not necessarily in the order in which they were conducted. Runs with differing compositions were often made on the same catalyst batch in order to level out the chances of any particular batch differing in activity from the others. The partial pressure of hydrogen was first kept constant at about 0.49 atmosphere, and that of carbon dioxide varied from 0.12 atm. to 0.49 atm.

While/

TABLE V.

TABLE V.

Catalyst - IB - 10% Ni - 3.1% ThO_2

" volume - 8.2 ccs.

Expt. No.	Time of Run mins.	Synth. Gas. Compsn. %				Product Gas Compsn. %					Weight of Cat. gms.	Temp. °C.	Rate of Flow. ccs./min.	Ccs.CO_2 convtd. /cc.cat. /min.
		CO_2	H_2	O_2	N_2	CO_2	H_2	CH_4	O_2	N_2				
25	6.6	12.0	48.3	0.3	39.4	10.6	39.4	4.2	0.4	45.4	5.62	280	593	2.17
26	5.1	11.9	48.4	0.3	39.4	11.1	43.4	2.96	0.2	42.3	"	280	784	2.41
27	12.6	11.8	48.4	0.3	39.5	9.7	35.3	6.6	0.2	49.2	"	282	308	1.63
28	12.2	24.0	49.6	0.4	26.0	23.6	37.2	7.4	0.3	31.5	5.62	280	320	2.08
29	5.1	24.0	49.6	0.6	25.8	23.7	39.6	5.0	0.6	31.1	"	285	784	3.78
30	5.5	25.0	49.0	0.5	25.5	23.5	40.3	4.7	0.3	31.2	5.28+	285	721	3.34
31	5.4	36.2	49.7	0.6	13.5	37.3	44.8	3.6	0.3	14.0	5.62	285	740	2.67
32	6.75	35.9	50.6	0.4	13.1	39.7	25.7	12.3	0.2	22.1	5.52	300	592	6.04
33	12.6	36.0	49.7	0.6	13.7	39.3	34.6	8.1	0.2	17.8	"	285	318	2.11
34	5.5	36.5	49.6	0.7	13.2	37.5	43.0	3.3	0.2	16.0	5.28+	285	727	2.74
35	5.7	36.1	49.0	0.5	14.4	36.0	40.9	4.6	0.3	18.2	"	288	702	3.54
36	8.25	36.0	49.2	0.6	14.2	38.4	39.8	4.8	0.8	16.2	"	285	485	2.40

TABLE V A

Expt. No.	Carbon dioxide Balance				Recovery %
	In Gas Collected			In Gas Passed	
	As CH_4 c.cs.	As CO_2 c.cs.	Total c.cs.	c.cs.	
25	120	301	421	464	91
26	101	377	478	477	100
27	174	258	442	460	96.2
28	213	685	898	935	96.2
29	158	749	907	939	97.0
30	170	850	1020	1000	102.0
31	118	1214	1332	1446	92.0
32	335	1082	1417	1437	98.6
33	218	1063	1281	1400	92.0
34	123	1382	1505	1460	103.0
35	165	1300	1465	1444	103.0
36	162	1275	1438	1440	100.0

TABLE VI.

TABLE VI.

Catalyst - IB. - 10% Ni 3.1% ThO_2

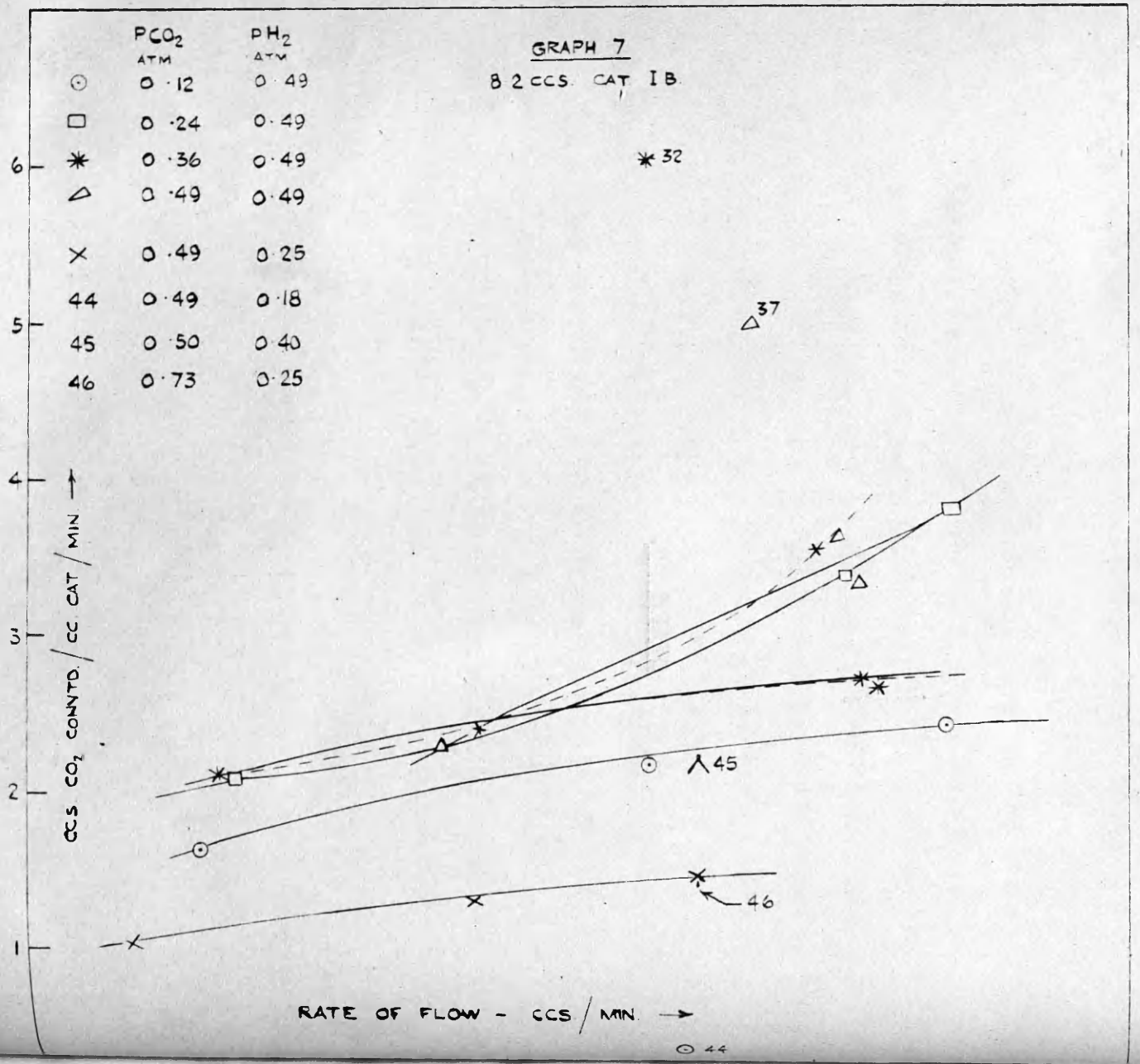
" Volume - 8.2 ccs.

Expt. No.	Time of Run. mins.	Synth. Gas Compsn. %				Product Gas Compsn. %					Weight of Cat. gms.	Temp. °C.	Rate of Flow ccs/min.	Ccs. CO_2 converted cc.cat./min.
		CO_2	H_2	O_2	N_2	CO_2	H_2	CH_4	O_2	N_2				
37	6.1	49.0	50.3	0.2	0.5	52.1	41.7	4.60	0.2	1.4	5.39°	290	658	5.00
38	5.6	49.6	49.0	0.2	1.2	50.9	40.6	4.72	0.5	3.2	5.28+	288	714	3.68
39	5.5	48.5	49.8	0.7	1.0	53.5	40.2	4.40	0.5	1.3	"	288	727	3.33
40	8.7	49.5	49.3	0.2	1.0	54.1	39.0	4.86	0.3	1.7	"	285	460	2.30
41	6.4	48.5	25.0	0.6	25.9	50.3	19.1	2.04	0.2	28.4	5.39°	283	625	1.45
42	15.1	49.0	24.0	0.4	26.6	51.0	14.2	3.60	0.4	30.8	"	284	265	1.04
43	8.3	49.0	25.0	0.5	25.5	51.8	17.5	2.60	0.6	27.5	5.30	285	482	1.30
44	6.5	48.0	18.7	0.6	32.7	49.6	16.3	0.33	0.6	33.2	"	283	615	0.24
45	6.4	50.4	40.4	0.6	8.6	53.8	32.5	3.28	0.5	9.92	5.39°	288	721	2.25
46	6.4	73.0	25.0	0.6	1.4	75.4	20.2	1.90	0.4	2.0	"	283	625	1.40

TABLE VI A.

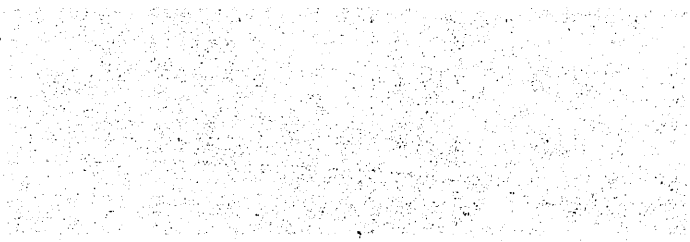
Expt. No.	Carbon dioxide Balance. In Gas Collected. As CH_4 c.cs.	As CO_2 c.cs.	Total c.cs.	In Gas Passed. c.cs.	Recovery %
37	161	1813	1974	1948	101
38	169	1827	1996	1984	99.4
39	150	1820	1970	1941	101.5
40	162	1800	1962	1980	99.0
41	76	1889	1965	1936	101.5
42	129	1810	1939	1952	99.3
43	93	1855	1948	1960	99.5
44	12	1884	1896	1905	99.5
45	118	1885	2003	2016	99.4
46	73	2866	2939	2958	99.4

GRAPH 7.

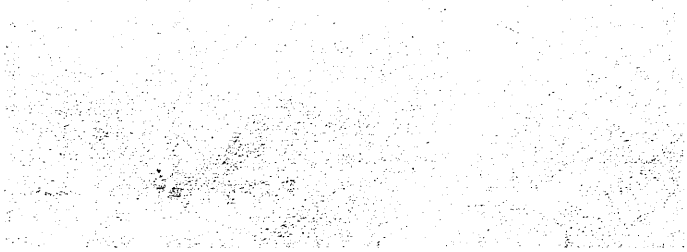

GRAPH 7
8 2 CCS. CAT I B
PCO_2 ATM
PH_2 ATM
⊙ 0·12 0·49
□ 0·24 0·49
✱ 0·36 0·49
△ 0·49 0·49
× 0·49 0·25
44 0·49 0·18
45 0·50 0·40
46 0·73 0·25
✱32
△37
⊙ 45
46
CCS CO_2 CONTD. / CC CAT / MIN →
RATE OF FLOW - CCS / MIN →
⊙ 44

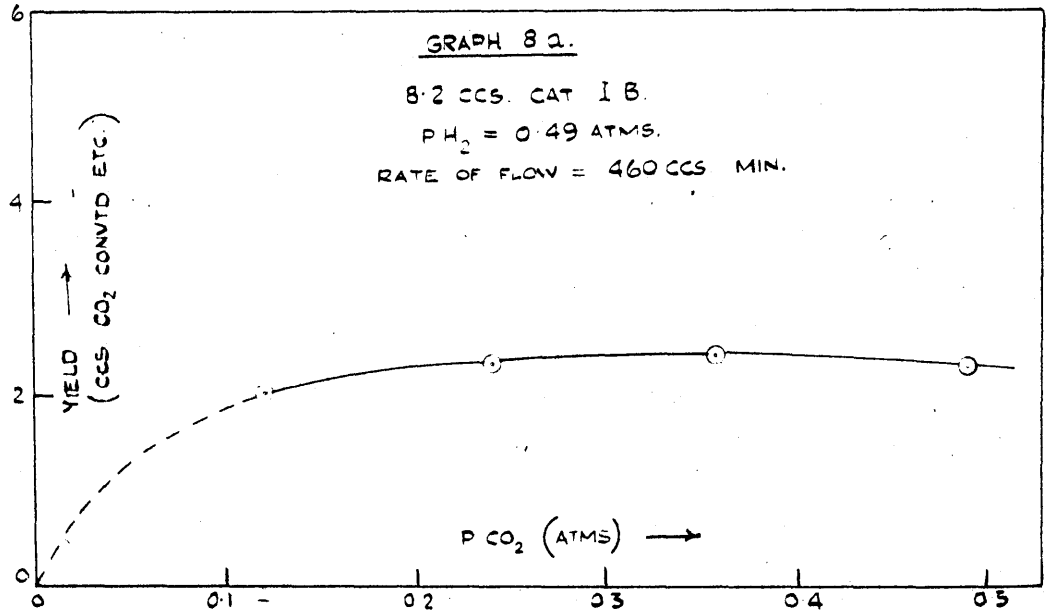
While the curves for pCO_2 = 0.12 and 0.24 atm. followed a regular course as is shown in Graph 7, some difficulty was experienced in the case of pCO_2 = 0.36 atm. and 0.49 atm. With a particular catalyst batch, points 32 and 37, corresponding to pCO_2 = 0.36 atm. and 0.49 atm. respectively, gave unusually high yields. The temperatures were high also. (290-300°C). It is unfortunate that no confirmation of these values were obtained. However, the values are obviously abnormal and may be rejected. It then appears that the reaction rate reached a limit with pCO_2 = 0.24 atm. after an initial rise from pCO_2 = 0.12 atm. At high rates of flow there also appears to be a fall at pCO_2 = 0.36 atm. In order to clarify the results, Table VII and Graphs 8a, 8b and 8c have been drawn up. They show the variation in reaction rate with varying pCO_2 at various rates of flow. It appears that the reaction rate reaches a limit and remains constant.

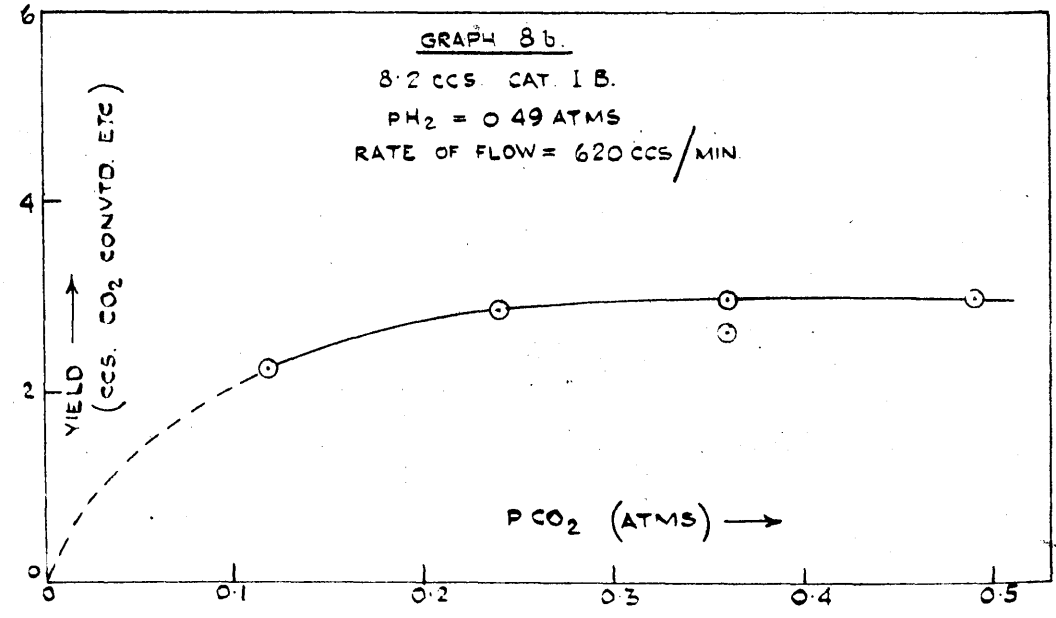
TABLE VII/

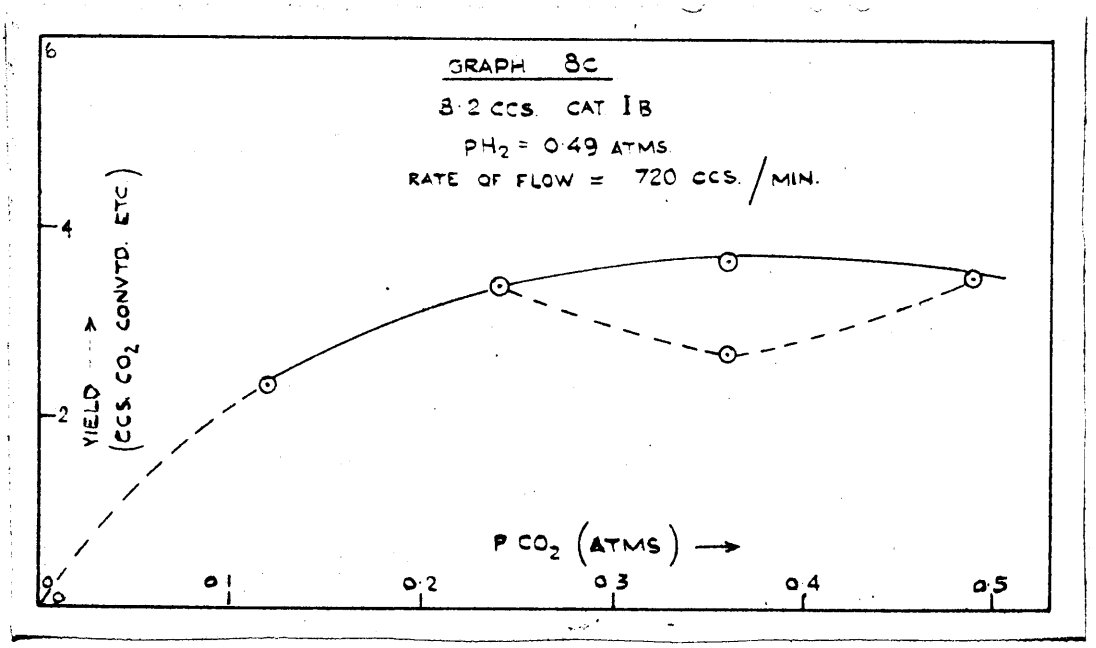


GRAPH 8 A and B.




GRAPH 8 a.
8·2 CCS. CAT I B.
$P H_2$ = 0·49 ATMS.
RATE OF FLOW = 460 CCS MIN.
YIELD (CCS CO_2 CONVTD ETC.)
$P CO_2$ (ATMS)
0
2
4
6
0·1
0·2
0·3
0·4
0·5


GRAPH 8 b.
8·2 CCS. CAT I B.
$P H_2$ = 0·49 ATMS
RATE OF FLOW = 620 CCS/MIN.
YIELD (CCS. CO_2 CONVTD. ETC)
$P CO_2$ (ATMS)
0
2
4
6
0·1
0·2
0·3
0·4
0·5


GRAPH 8c
8·2 CCS. CAT I B
PH_2 = 0·49 ATMS.
RATE OF FLOW = 720 CCS. / MIN.
YIELD → (CCS. CO_2 CONVTD. ETC.)
6
4
2
0
$P\,CO_2$ (ATMS) →
0·1
0·2
0·3
0·4
0·5

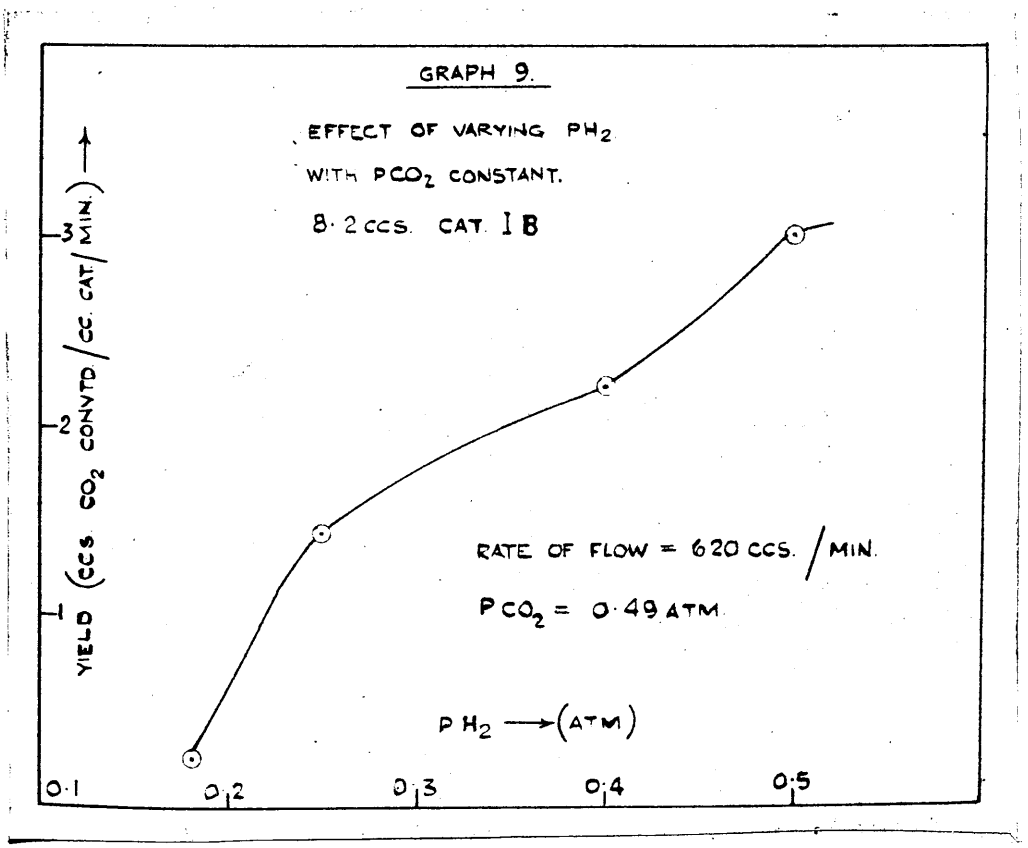

GRAPH 9.
EFFECT OF VARYING PH_2
WITH PCO_2 CONSTANT.
8·2 CCS. CAT I B
YIELD (CCS. CO_2 CONVTD / CC. CAT / MIN.) →
3
2
1
RATE OF FLOW = 620 CCS. / MIN.
PCO_2 = 0·49 ATM.
$P\,H_2$ → (ATM)
0·1
0·2
0·3
0·4
0·5

TABLE VII.

Synth. Gas.		Yields at rates of flow = (ccs./min.)		
pCO_2 atm.	pH_2 atm.	460	620	720
0.12	0.49	2.0	2.24	2.36
0.24	0.49	2.3	2.86	3.40
0.36	0.49	2.4	2.98 2.62	2.7 3.7
0.49	0.49	2.3	3.0	3.45
0.50	0.40	-	2.22	-
0.49	0.25	-	1.45	-
0.49	0.18	-	0.24	-

In a similar way the partial pressure of carbon dioxide was kept constant at 0.49 atm. and that of hydrogen varied from 0.18 to 0.49 atm. All the runs were made at a rate of flow of about 620 ccs./min., or a space velocity of 4500 (ccs./cc.cat./hr). In this case, there was an almost regular rise as pH_2 was increased from 0.18 to 0.49 atm., as is shown in Graph 9.

From/

From these results it appears that both reactants are adsorbed on the catalyst surface. When the partial pressure of hydrogen is high it occupies more of the surface, but as more carbon dioxide is introduced, some of the hydrogen is displaced yielding more space for carbon dioxide. The reaction rate is at its highest when some arbitrary ratio between the respective adsorptions is reached. After that, as long as the hydrogen pressure is kept constant at 0.49 atm., further increase in carbon dioxide has no effect. When the partial pressure of carbon dioxide is fixed, the reaction rate goes on increasing as more hydrogen is introduced showing that hydrogen adsorption is the limiting factor under these conditions and carbon dioxide is strongly adsorbed.

These general conclusions are in agreement with those put forward by Nicolai and others, (58) who studied the reaction under static conditions and found that both the reactants are weakly adsorbed on a nickel catalyst and that carbon dioxide is more strongly adsorbed than hydrogen.

It was next considered necessary to extend these studies to pressures above atmospheric. Under such conditions, it would not be necessary to introduce a third gas in order to vary the partial pressure of either reactant with respect to the other.

****

PART II.

THE INTERACTION OF CARBON DIOXIDE AND HYDROGEN ON NICKEL CATALYSTS AT PRESSURES ABOVE ATMOSPHERIC.

CHAPTER I.

DESCRIPTION AND LAYOUT OF PLANT.

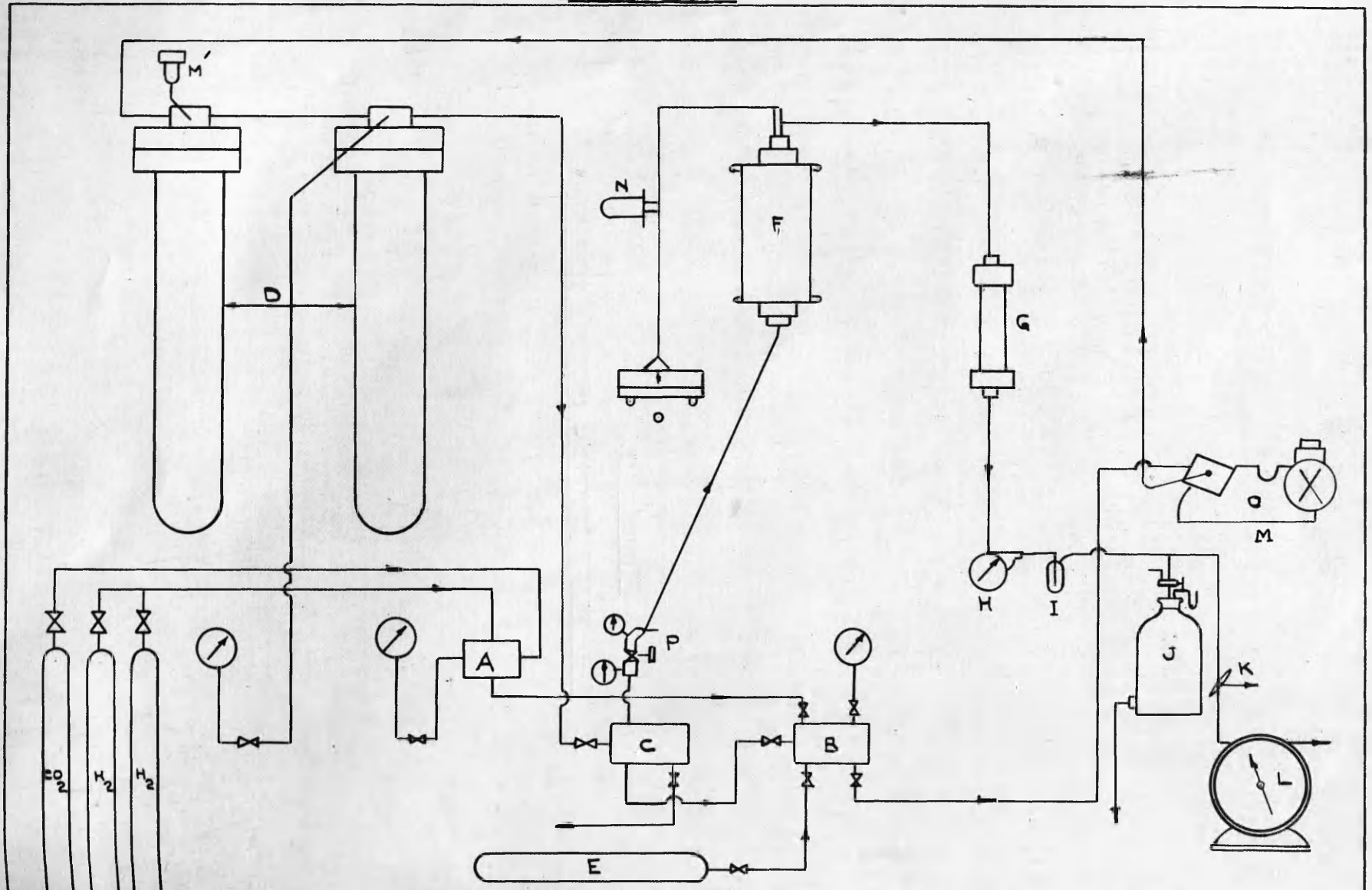
The object of the experiments to be described in this section was to study the effect of the variation of partial pressures of the reactants, carbon dioxide and hydrogen, under pressures ranging up to about 250 lbs/in.^{2} No special high pressure equipment was therefore necessary. However, suitable equipment for mixing large quantities of gas under atmospheric pressure and then compressing them to the pressures required, were not available. It was therefore found necessary to make use of parts of an existing high pressure circulating plant, to mix and store gases under pressure. Synthesis mixtures could then be tapped from the storage after suitable pressure reduction and fed on to the reaction system.

The existing plant had been used some time ago for studies on the synthesis of methanol. It consisted of two high pressure storage cylinders which were connected to a high pressure circulating pump, via several pressure blocks and valves. A high pressure reaction vessel, condenser and product receiver were connected to the main circulatory system in such a way as to enable unreacted gases to be recirculated. Since this arrangement was not suitable for the purpose in view, the entire plant had to be dismantled, overhauled and reassembled with/

FIGURE 1.

H.P. PLANT LAYOUT - GENERAL SCHEME.

FIGURE 1.



H.P. PLANT LAYOUT - GENERAL SCHEME.

with suitable changes in design and addition of new units and connections.

Layout of Plant.

The layout of the plant is first explained followed by a detailed description of the important units. The general scheme of the final plant layout is shown in Figure 1. From the supply cylinders of carbon dioxide and hydrogen, the gases are introduced into the system via the feed block A and the low pressure block B. From block B, the entering gases pass on to a high pressure circulating pump M, the discharge end of which is connected to two high pressure storage cylinders D. When the requisite amounts of the two reactants, as measured by the pressure gauges, have been introduced into the storage cylinders, the supply is cut off. The high pressure block C is then put in communication with the low pressure block and the storage cylinders; the stored gas is then allowed to mix by circulation. The path traversed is now from the storage cylinders, through blocks C and B to the circulating pump and back to the cylinders. One of the storage cylinders is provided with a safety valve M′ while the other has a pressure gauge attached to it.

The gas mixture is then sampled through one of the extra connections on the pressure blocks and analysed to find whether proper mixing has occurred; if mixing is found satisfactory/

satisfactory, the gas is fed on to the reaction chamber F, through a pressure regulator P. The reaction chamber is heated by an electric furnace. The temperature in the catalyst bed is measured by a thermocouple, which is connected to a millivoltmeter O, via the cold junction thermos flask N.

From the reaction chamber F, the product gas passes on to a drying tube G containing silica gel. The water of reaction is thus removed and the partially dried gas is then let out to atmospheric pressure by the reducing valve H. The outflowing gas is passed through a glass bubbler I and measured by a wet gas meter L. In between, a portion of the flowing product gas is continuously sampled into a sampling aspirator J, provided with a two-way stopcock and a water manometer, which serves to ensure a constant rate of sampling. The two-way stopcock K is provided in order to enable the gas meter to be by-passed immediately before and after a run is recorded. For the testing of leaks etc., a nitrogen cylinder E is connected to the low pressure block when required. Details of the actual experimental procedure have been recorded in a subsequent chapter.

The storage cylinder, the reaction chamber, the drying tube and the supply block A, are all housed in a steel cubicle. The high and low pressure blocks, pressure regulator, reducing and interconnecting valves, pressure gauges, millivoltmeter, rheostat for the furnace, switches for the pump, furnace and lights are all mounted in front of the cubicle, which /

FIGURE 2.

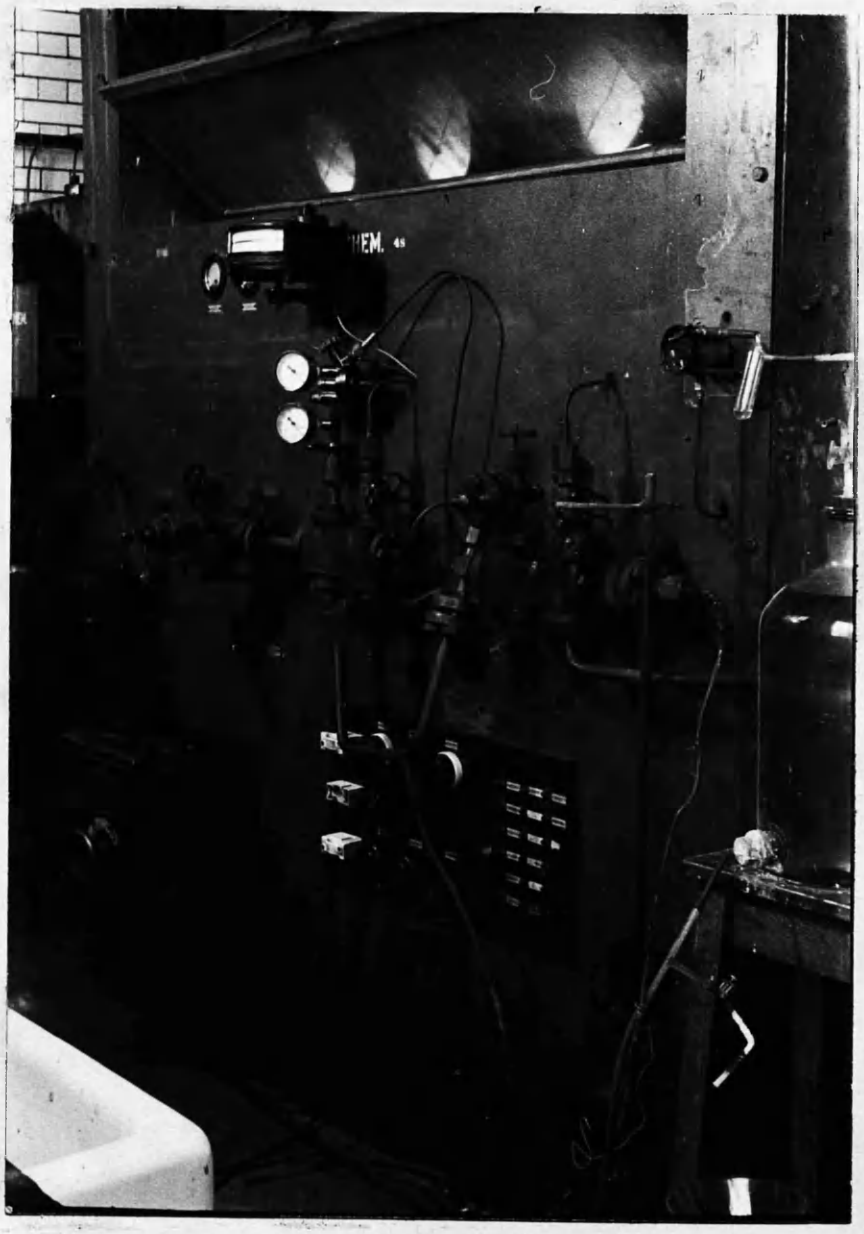
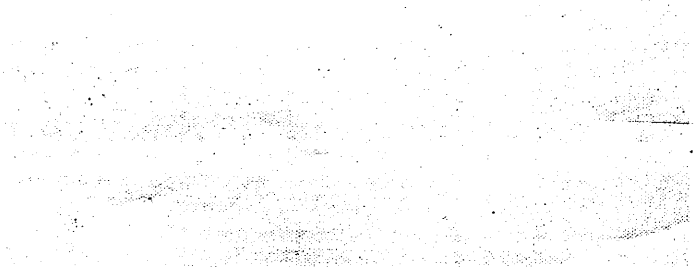


FIGURE 2.

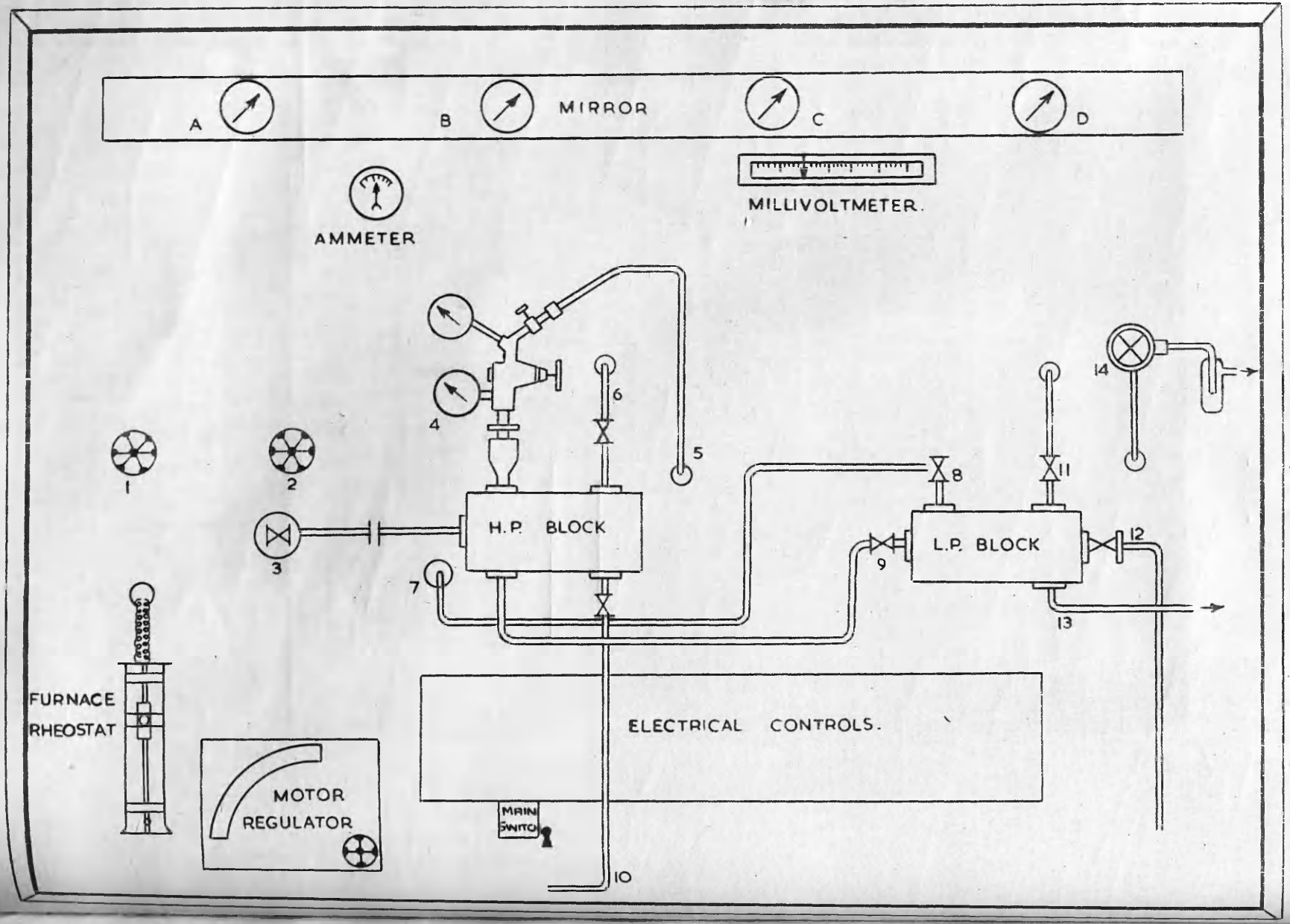
FIGURE 3.

CONTROL PANEL.



CONTROL PANEL

FIGURE 3.



which thus constitutes the control panel. The circulating pump and motor are fixed on a bed outside the cubicle, while the supply cylinders are supported against one side of the cubicle.

DETAILS OF PLANT.

Cubicle and Control Panel.

A front view of the cubicle consisting of the control panel is shown in Figure 2. The panel arrangement is illustrated diagrammatically in Figure 3.

A, B, C and D are Budenberg pressure gauges mounted in a steel-box fitted with a chromium-plated mirror. The gauges are viewed in the mirror, being a safety measure in case any of the gauges blow out. The gauges, controlled by valves 1, 2, 6 and 11, respectively indicate the pressures in the storage cylinders, supply cylinders (via feed block), H.P. block and L.P. block.

The tube connecting the feed block (which is inside the cubicle) to the L.P. block comes out on to the control panel through an opening 7, and leads on to an I.C.I. needle valve 8, mounted on the L.P. block. The H.P. and L.P. blocks are connected through another needle valve 9. By opening the high pressure Hopkinson valve 3, connection is made between the storage cylinders and the H.P. block. From the H.P. block, the gases are fed on to the reaction chamber (which is housed within/

FIGURE 4.

FIGURE 4.

within the cubicle) through the pressure regulator 4 and the opening 5. The outlet tube from the reaction chamber is brought back to the control panel and to the reducing valve 14 through another opening. Connection 13 on the L.P. block leads to the circulating pump, while connection 12 is meant either for sampling or for connecting a test cylinder to the system.

The ammeter records the current in the furnace for the reaction chamber; the current is controlled by a rheostat mounted on the panel. The motor regulator is for the circulating pump, while the electrical controls consist of fuses and mainly switches for furnace, motor, thermocouple and lights.

Cubicle.

The cubicle itself is 6 feet 2 inches long, 4 feet 7 inches broad and 7 feet high. The lower parts of the sides and back are covered with expanded metal screens with welded-on edges; the upper portions consist of 3/16 inch sheet metal. The control panel is a 1/4 inch steel sheet. These are fixed to the framework by studs and wing nuts.

Figure 4 shows the manner in which the gas supply cylinders are held against the side of the cubicle. Two hydrogen cylinders are connected in parallel by means of a two-cylinder coiled type coupler and adaptors. The pipe line from/

FIGURE 5.

STORAGE CYLINDER A.

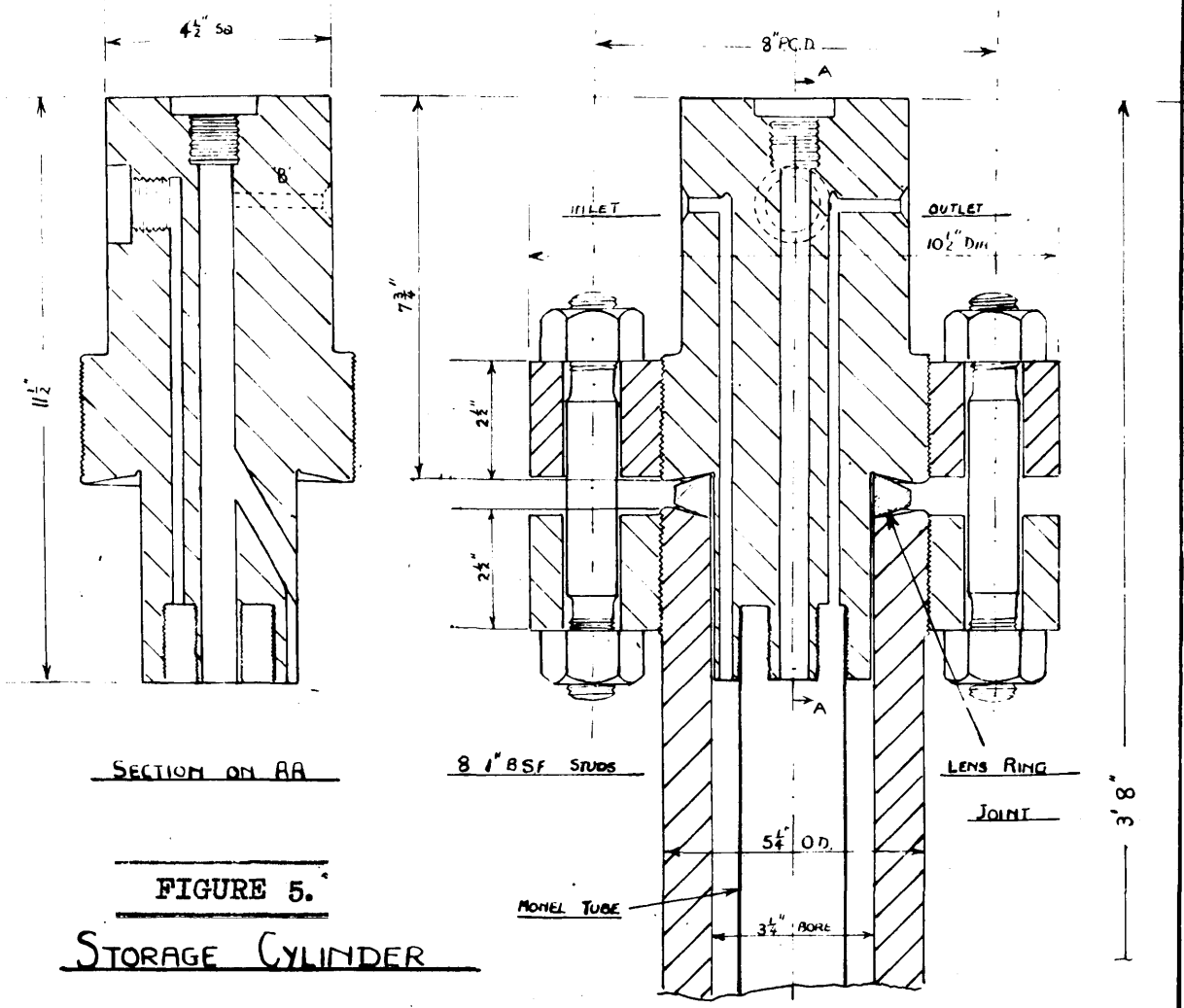


FIGURE 5.

STORAGE CYLINDER

from the CO_2 cylinder is connected to it by a specially made pressure union with a copper gasket.

STORAGE CYLINDERS.

These cylinders were originally designed as preheater and reaction vessel. They were later adapted to serve the purpose of storage cylinders. A drawing of one of these cylinders is shown in Figure 5 and both are identical in design. Each cylinder is made of a special 5.5 per cent. chrome steel alloy and consists of a cover block resting on a large lens ring seated on the main body. The cover block and the body are provided with threaded-on flanges, which enable the block to be held firmly on to the body by means of eight 1 inch studs, arranged on a P.c.D. of 8 inches. The lens ring provides a gas-tight joint.

The cover block carries five holes in all. The two large holes shown in the sectional view of the cover block alone are not required and are sealed with screwed-in steel plugs seated on annealed copper rings. The fifth hole shown at "B" in the sectional view on AA, is connected in one case, to a safety valve, while in the other cylinder, a connection from this leads to a pressure gauge.

The bottom of the cover block carries a screwed-in monel tube. From the drawing, it is seen that the entering gas has/

FIGURE 6.

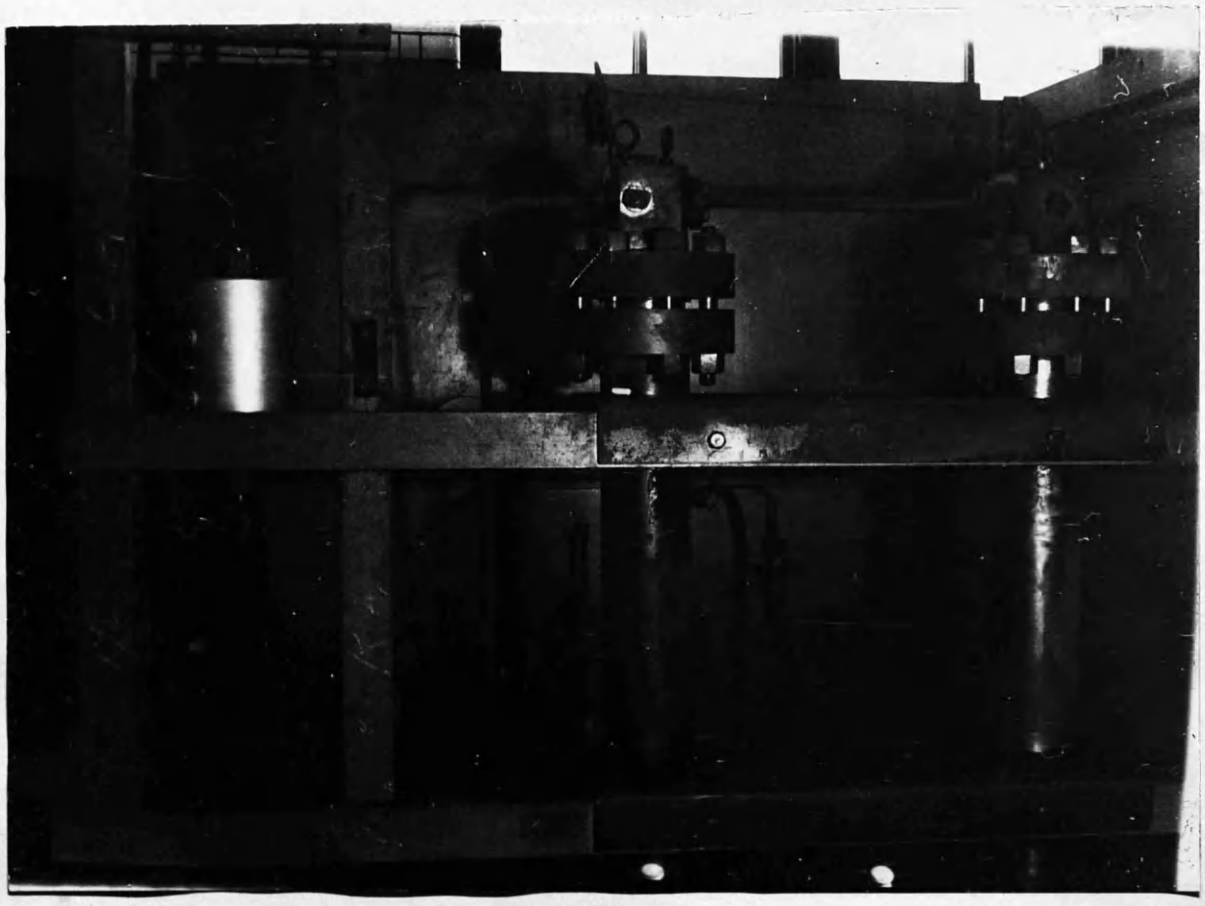
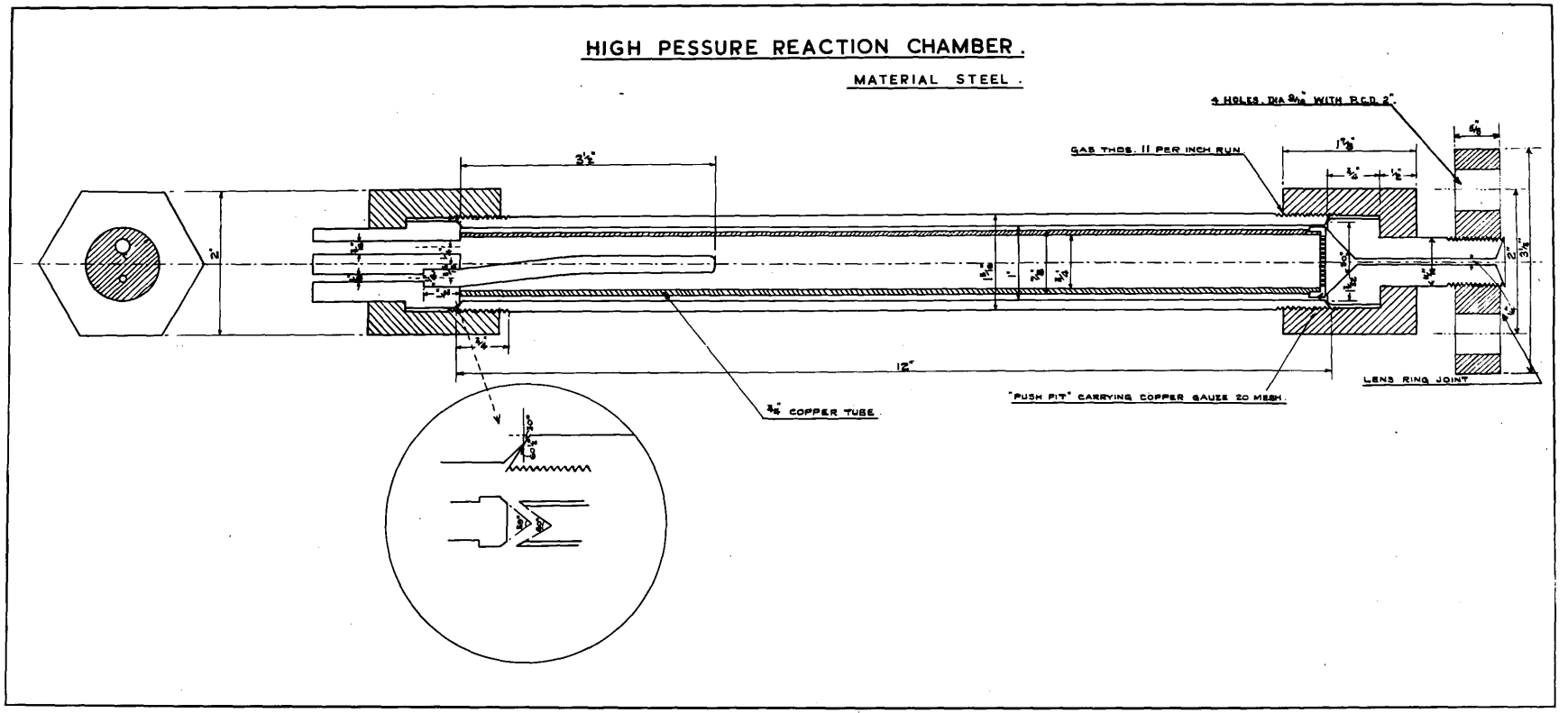


FIGURE 6.

FIGURE 7.

HIGH PRESSURE REACTION CHAMBER.

FIGURE 7.


HIGH PESSURE REACTION CHAMBER.
MATERIAL STEEL.
4 HOLES. DIA 9/16" WITH P.C.D. 2".
GAS THDS. 11 PER INCH RUN
2½"
12"
¼" COPPER TUBE
"PUSH FIT" CARRYING COPPER GAUZE 20 MESH.
LENS RING JOINT

has to pass to the bottom of the cylinder through the annular space between the cylinder and the monel tube before it passes up the tube to the outlet. This arrangement, plus the existence of spiralled grooves on the monel tube is expected to ensure complete circulation and mixing of the gas.

A view of the cylinders in position, as seen from the back of the cubicle is shown in Figure 6. Only the supporting brackets and girders are visible in the photograph, but the cylinders actually rest on brass castings supported by another horizontal girder.

REACTION CHAMBER.

The reaction chamber was specially designed and fabricated to suit the purpose and a drawing of it is shown in Figure 7. The left-hand side of the drawing represents the top of the chamber. It consists of a steel tube (1 inch I.D. and 1.5/16 inches O.D.) with gas threads cut at either end to carry union nuts. The union heads or nipples at either end are designed on the cone-joint principle. The top head carries two holes of 3/16 inch and 1/8 inch bore. The 1/8 inch hole is widened to 1/4 inch at the inside end and into it a thermocouple pocket is screwed in and gas welded. The thermocouple pocket is off-set so as to be at the centre of the reaction chamber. The 3/16 inch hole is threaded at the outside/

FIGURE 8.

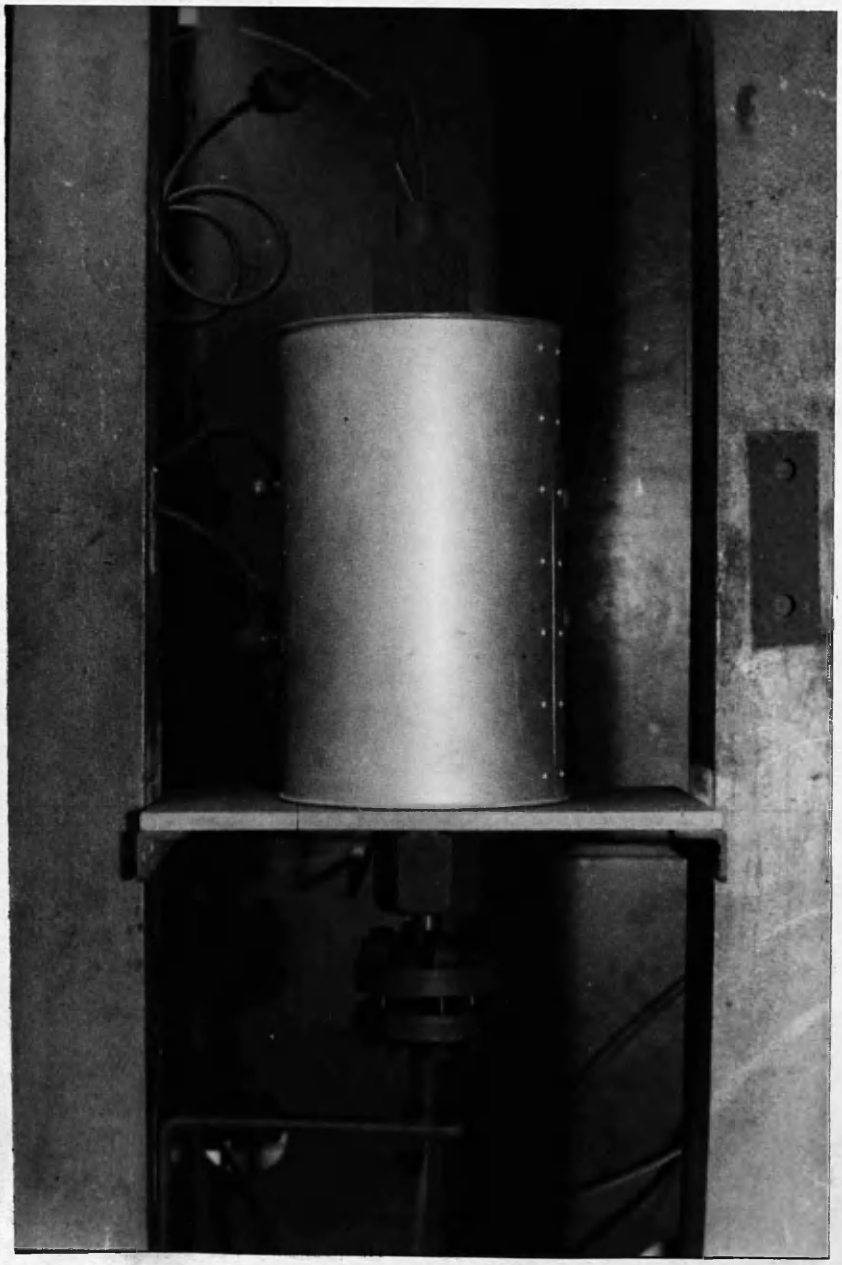


FIGURE 8.

FIGURE 9.

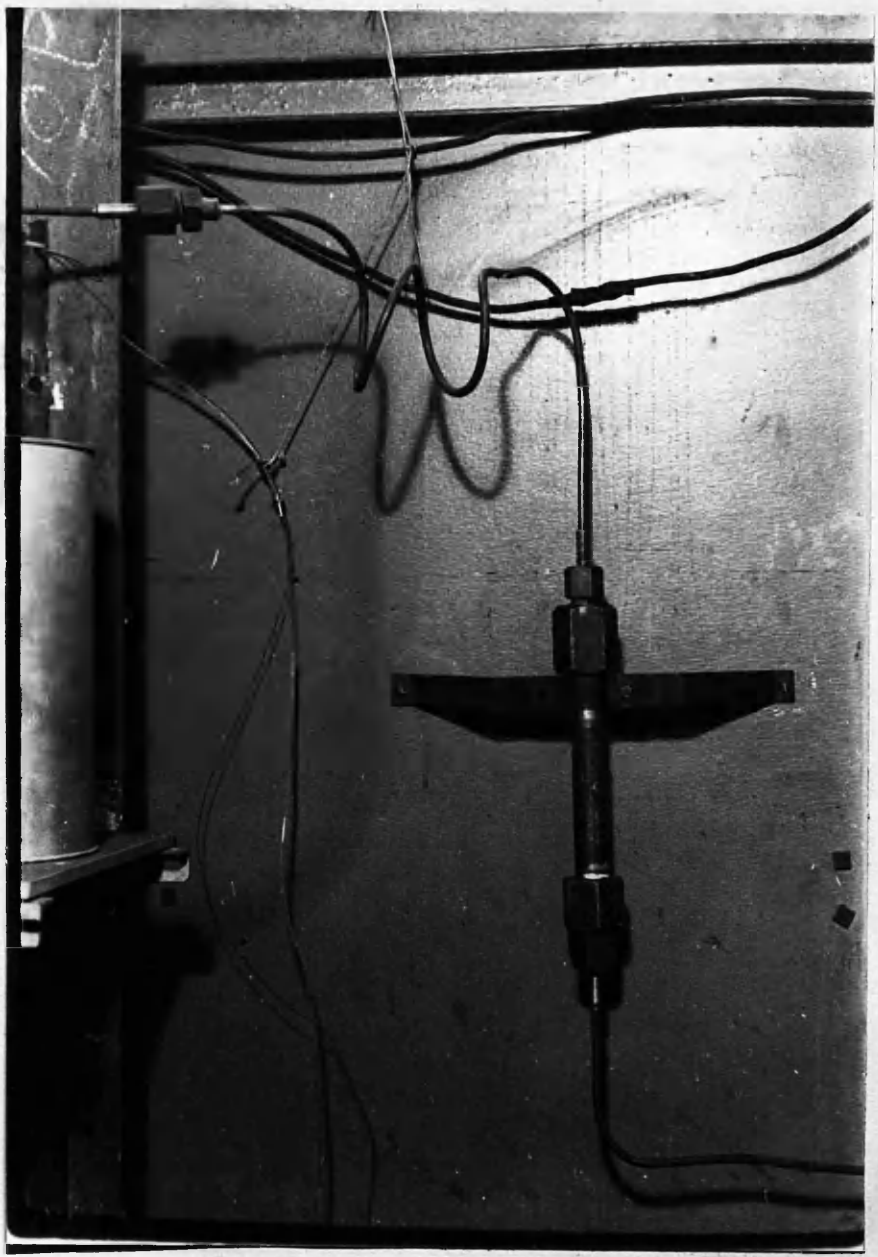


FIGURE 9.

outside end to receive one end of a steel pressure tube, which is screwed in and welded, the other end of the tube being connected to the drying tube by means of a union coupling.

The bottom head of the chamber carries a limb to which a flange is attached. This permits of a lens ring connection to a pressure tubing leading from the pressure regulator.

A copper tube of 3/4 inch I.D. is placed co-axially with the outer tube and is held in position by a tight fit into a circular recess on the top union head. The lower end of the copper tube is closed with a push-fit perforated copper cap. (20 mesh). The lower half of the tube is filled with pumice and serves as the preheating zone, while the upper half contains the catalyst spread around the thermocouple pocket. Figure 8 shows the reaction chamber assembled in position on a bracket together with the electric furnace.

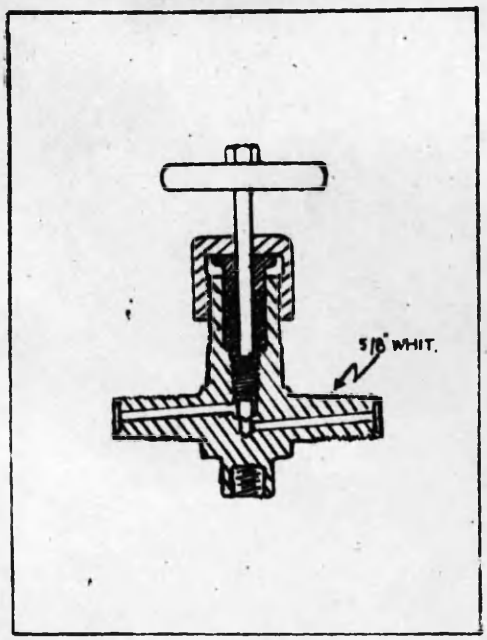
DRYING TUBE.

The drying tube was refashioned from a steel tube 8 inches long, with a 1/2 inch bore and of 1 inch O.D. The connections to pressure tubing at both ends are by union and nipple couplings with copper gaskets. The drying tube with its connections is illustrated in Figure 9.

PRESSURE/

FIGURES 10 AND 12.

FIGURE 10.



FINE-ADJUSTMENT VALVE.
[I.C.I. TYPE]

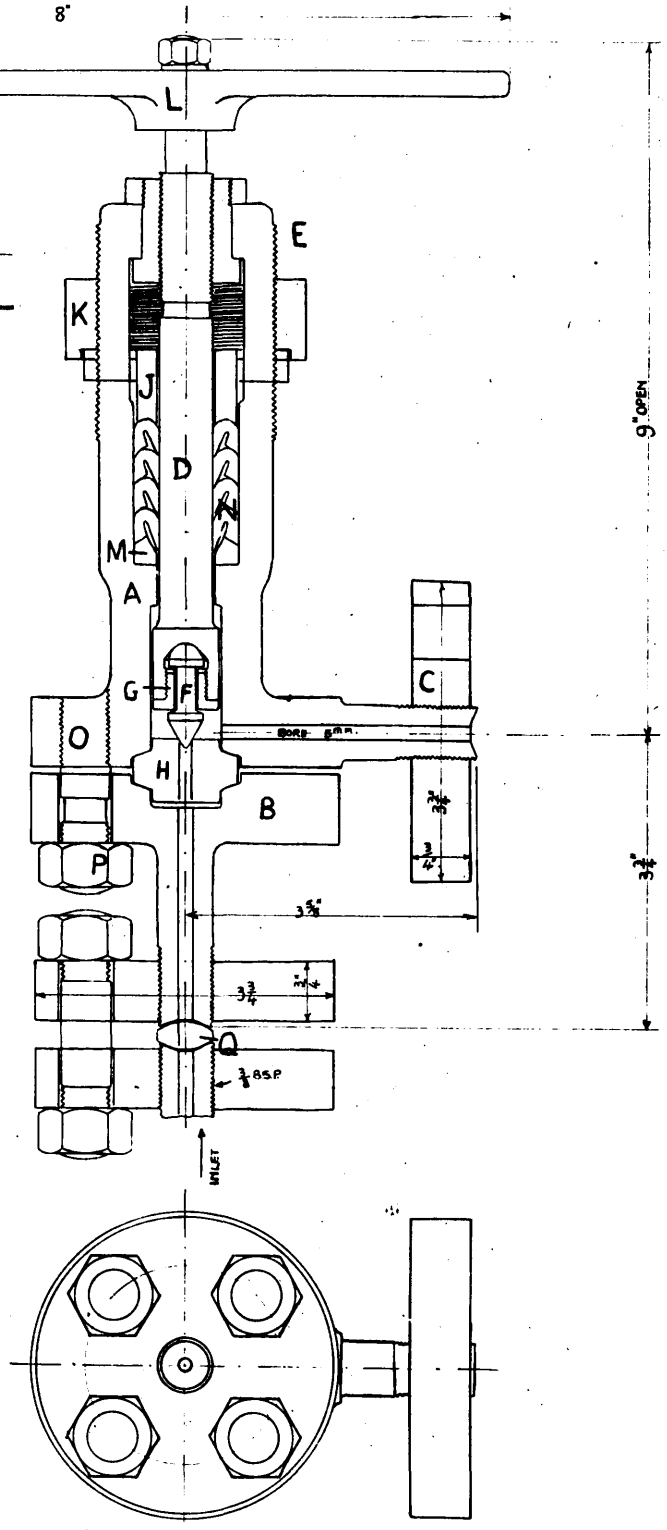
FIGURE 12.

FIGURE 11.

HOPKINSONS HIGH PRESSURE STOP VALVE.

FIGURE 11.

REF	NAME	MAT	N°
A	BODY (TOP HALF)	MS	1
B	" (BOTT ")	"	1
C	FLANGES	"	4
D	SPINDLE	SS	1
E	" BUSH	GR	1
F	VALVE	[illegible]	1
G	" NUT	SS	1
H	SEAT	PLAT ING	1
I	----	---	---
J	GLAND	MS	1
K	" NUT	"	1
L	LEVER	"	1
M	PACKING RING	SS	1
N	SPRING		
O	STUDS	HIGH TENSILE	4
P	NUTS	MS	4
Q	LENS RING	SS	2



VIEW LOOKING ON INLET

HOPKINSONS HIGH PRESSURE
STOP VALVE

PRESSURE REGULATOR.

This is a standard oxygen regulator carrying two pressure gauges, one reading up to 200 atmospheres, while the other is calibrated to read up to 400 lbs/inch.^{2} The regulator is connected to the H.P. block through an adaptor and a lens ring joint. The adaptor is illustrated in Figure 10.

CIRCULATING PUMP.

The circulating pump and driving motor are mounted on a wooden stand. It is a reciprocating pump of 5/8 inch bore and is capable of circulating 60 litres of gas per hour at a maximum speed of 330 r.p.m.

VALVES, PIPE LINES, JOINTS, GAUGES.

A Hopkinson's high pressure valve, shown in Figure 11, connects the storage cylinders to the H.P. block. The valve needle and seat are of platnam alloy. The other needle valves employed are of the I.C.I. fine adjustment type shown in Figure 12, and contains soft lead washers as gland packing.

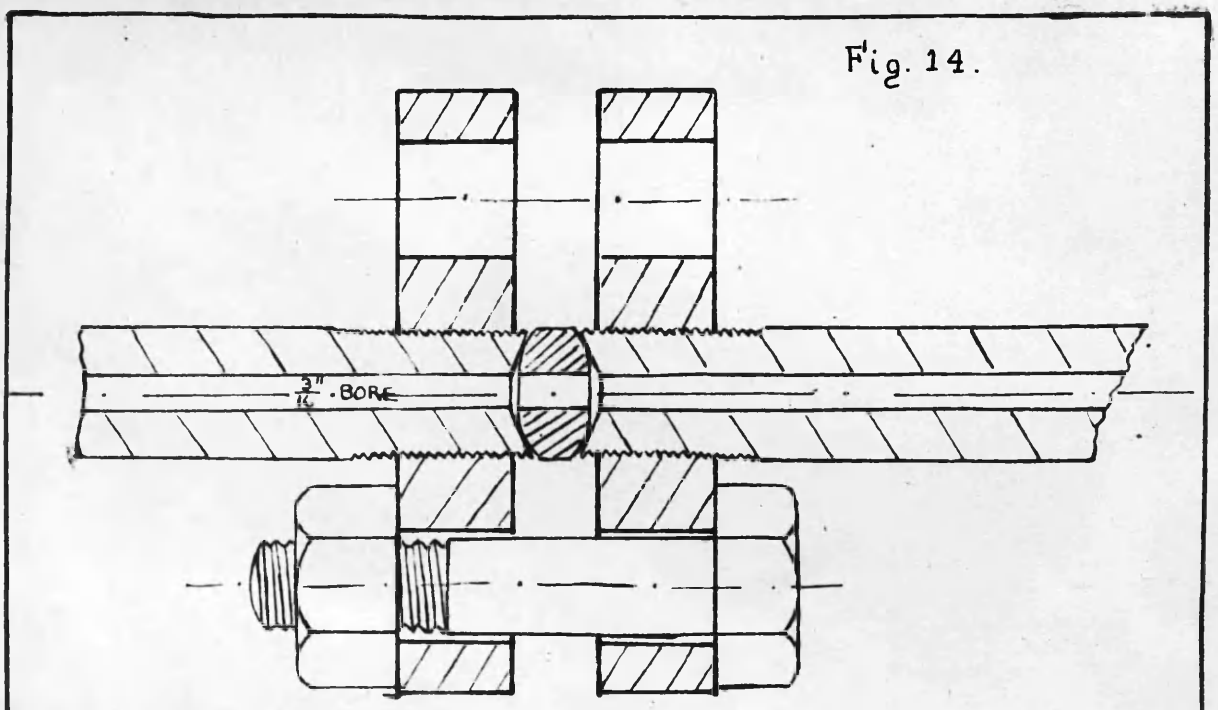
The final outlet reducing valve is an R.A.F. oxygen cylinder valve shown in Figure 13. It has a pressure recording dial in front and a spring-loaded adjustable diaphragm at the back. There is a spring-loaded safety valve on one side.

The/

FIGURES 13 AND 14.

FIGURE 13.

Fig. 14.



LENS RING JOINT

The outflow is controlled by a small needle valve and the inlet end accommodates a brass union coupling.

The pipe lines connecting the gauges, supply cylinders and reaction system consist of 6 per cent Cr, 6 per cent. Ni high pressure steel tubing of 1/16 inch bore and 1/4 inch O.D. These are connected by bronze unions or screwed into short lengths of pipe suitable for an I.C.I. type of lens ring joint, shown in Figure 14. Other pipe lines are of high pressure steel tubing of 3/16 inch bore and 11/16 inch O.D. connected by lens ring joints.

The Budenburg steel pressure gauges used are capable of recording up to 6000 lbs/inch.^{2}

Some of the difficulties encountered during the operation of this plant are described in the following chapter. The main source of trouble at a later stage was the outlet valve, which gave satisfactory performance only for a short time. Repeated breakdowns occurred owing to accumulation of moisture and leakage through the diaphragm and safety valve contained in it. Constant repairs and replacements had to be made resulting in considerable amount of delay and interruption.

It is suggested that for future work on this plant, this valve and its connections be entirely replaced by some other type of valve. It is also suggested that for a reaction where condensible products are formed, the drying tube be preceded by a suitable condenser.

****

CHAPTER II.

TESTING OF PLANT AND EXPERIMENTAL PROCEDURE.

After the plant had been assembled, it was tested for leaks with nitrogen from a test cylinder. Nitrogen was first introduced into the system up to a pressure of about 50 atmospheres. Even at these pressures leaks were detected in several lens ring joints. The joints were therefore opened out and refitted. In such joints, proper alignment of the rings is desirable and where the rings have to be introduced vertically, the process is particularly difficult. Rings with a groove around the edge were procured and while fitting, were held rigid by a stiff wire around the edge.

Each section of the plant was then isolated from the others by means of the valves attached and tested for leaks. The Hopkinson's high pressure valve was found to be working unsatisfactorily when completely shut. It was therefore dismantled and the fault was traced to the valve piece which had worn out. Regrinding of the valve proved unsatisfactory and it had to be finally replaced. It was then found that the pressure gauge attached to the low pressure block registered a steady fall from 70 atmospheres when the block was isolated. The fall in pressure was noticeable even at 20 atmospheres. This block carried five lens ring joints and when tested each of these was found satisfactory. It was

then/

then assumed that the fault lay in the pressure gauge itself or in one of the joints leading up to it. Having failed to detect any obvious leaks, it was decided to seal off the gauge by closing the gauge valve completely.

The two high pressure storage cylinders were then isolated and found to be leaking as shown by a gradual pressure drop in the gauge attached to the second cylinder. It was essential that at least this portion of the plant be leak proof, otherwise there would be no purpose in attempting to store gas under pressure. Mere tightening of all the cover studs in the two cylinders proved ineffective. The covers were then dismantled and the two large lens rings re-aligned and assembled. This gave better results although the leaks were not eliminated.

A leak at the pump gland was also found difficult to stop, but was reduced by tightening the gland nut. When the pump was running, pulsations on the L.P. block pressure gauge indicated that the pump valves were working satisfactorily and gas was being circulated. To test whether the passages to and from the pump were clear, nitrogen was introduced into the storage cylinders via the pump alone. The storage gauge indicated that the cylinders were being filled up.

The next problem was to obtain a mixture of carbon dioxide and hydrogen in the required proportions. The

nitrogen in the system was released to the atmosphere and carbon dioxide direct from the supply cylinder was first introduced followed by hydrogen, with the circulating pump running at about 200 r.p.m. Assuming that the circulating pump was working, it should circulate 46 litres/hour at 200 r.p.m. Since the volume of the plant was only about 7 litres, in three hours time the gases would have been circulated about twenty times and by then, complete mixing should have occurred. It was however found that the mixing was incomplete. The following are the analyses of samples of one mixture, tapped at various intervals of time. The pump was kept continually running and the gas was sampled through the valve and pipe line used for connecting the test cylinder.

Mixture as filled in:- CO_2 - 11 atmospheres.

H_2 - 22 atmospheres.

Samples:-

Time	CO_2%	
11.30 a.m.	1.3	
1.00 p.m.	2.2	
2.00 p.m.	4.8	
5.00 p.m.	12.0	(Pump stopped)
Next morning		
11.00 a.m.	37.0	

The above indicated that the pump was not working satisfactorily and that mixing by natural diffusion occurred on leaving/

leaving overnight. Furthermore, the total pressure in the system after 24 hours had fallen from 33 atms. to 20 atms., giving an average pressure drop of about 8 p.s.i./hour. It was therefore quite possible that with such an appreciable leak in the system, hydrogen would diffuse out in preference to carbon dioxide, and that the resulting rise in carbon dioxide content was due rather to loss of hydrogen than to natural mixing.

It was however decided to make a few trial runs with the existing arrangement, in order to establish experimental conditions and to modify procedure for future work. The reaction chamber (Figure 7 page 109) was first filled with the catalyst. The chamber head was held upside down and an asbestos paper sheath $2\frac{1}{2}$ inches long and of approximately the same diameter as the internal diameter of the copper liner, was placed on it around the thermocouple pocket. The sheath was then packed with alkali-free ignited asbestos wool, and the copper liner was slipped over it and into the groove. Twenty ccs. of Ni - ThO_2 catalyst I B. were then introduced into the liner and levelled by tapping. The arrangement was such that the end of the thermocouple pocket now lay midway in the catalyst mass. The rest of the liner was then filled with purified pumice and the perforated cover slipped on. The main body of the reaction chamber together with the bottom head/

head and the tube furnace were fixed in position on the appropriate bracket. The filled copper liner attached to the chamber head was then slipped in and the two nuts tighened, the final assembly being as shown in Figure 8. page 111). The thermocouple was introduced into the pocket. The couple wires were at first insulated with small bits of narrow silica tube. The pocket was extremely narrow, and being bent at the same time, it was found rather difficult to introduce and remove the thermocouple. Some bits of silica tubing would invariably break in the process, resulting in further sticking. At a later stage in the experimental work, the silica insulation was stripped off and in its place, the wires were carefully wound with glass fibres taken from a piece of glass cloth. This gave a thin, flexible and efficient insulation.

The catalyst was reduced for about 7 hours at a temperature of 290°C. and a hydrogen rate of about 8 litres/hour. A fresh synthesis mixture was made in the storage cylinders. Due to incomplete mixing, however, it was found that the gas composition varied with each run. Table I of this series summarises the results obtained from these preliminary runs. Following reduction, the catalyst temperature was brought down to a slightly lower value than that actually required and the synthesis mixture was introduced into the reaction chamber by operating/

operating the regulator valve on the H.P. block (Figure 3 page 102), until the second gauge in the valve showed the required pressure. Since this gauge was in direct communication with the reaction chamber, it was reasonable to assume that the pressure thus registered was the actual pressure in the reaction chamber. The regulating valve gave very satisfactory performance, and provided the supply pressure was high enough, it maintained a constant pressure in the reaction chamber irrespective of the rate of flow of the gas.

The rate of flow was adjusted by operating the outlet valve. The gas thus let down to atmospheric pressure, was bubbled through a small amount of dilute sulphuric acid or saturated brine. This served as a rough flow indicator. It was then sampled through a T-piece as it passed on to the wet gas flow meter. The sampling was done by means of an aspirator provided with a water manometer. As far as possible a constant rate of sampling was obtained throughout a run by maintaining a constant pressure difference in the manometer. Saturated brine was used in the aspirator. Each run was timed by a stop-watch. Before recording a run, the outflowing gases were allowed to saturate the water in the wet gas meter as far as possible, and some time was allowed for temperature adjustment. In the preliminary runs the temperatures recorded were/

were irregular.

The method in which the data were evaluated is shown by the following sample calculation. The calculation has been taken arbitrarily from experiments conducted under improved conditions.

Sample Calculation.

Time of run	-	16 mins.	Cat. Ni - ThO_2 I B.
Temp.	-	290°C.	Cat. volume - 20 ccs.
Reaction pressure	-	5.6 atms.	
Synthesis gas composition:	-	CO_2 - 49.5% H_2 - 50.0%	
Partial pressure of reactants:	-	pCO_2 = 2.8 atms. pH_2 = 2.8 atms.	
Gas let out (metered)	-	0.319 cu.ft.	at normal pressure and 20°C.
(sampled)	-	2.05 litres.	
Total	=	11.075 litres.	

Product gas composition:-

CO_2	-	54.2%
O_2	-	0.4
CO	-	0.8
CH_4	-	5.6
H_2	-	38.6
		99.6

From this composition, the composition of the synthesis gas may be calculated backwards:-

100/

100 ccs. of product gas accounts for:-

	CO_2	and	H_2	
(as CO_2)	54.2		38.6	(as H_2)
(as CO)	0.8			
(as CH_4)	$\frac{5.6}{60.6}$ ccs.		$\frac{4 \times 5.66}{61.24}$ ccs.	(from CH_4)

Total = 122.24 ccs. of CO_2 and H_2 of which 60.6 ccs. are CO_2 and 61.24 ccs. are H_2. Therefore, composition of the gas fed in must have been

CO_2 - 49.6% and H_2 - 50.0%

This composition is exactly the same as that found by actual analysis of the synthesis gas.

Now, volume of product gas let out

= 11.075 litres.

This will, therefore, be equivalent to 11.075 x 1.222 litres of synthesis gas. (Since 100 ccs. of product gas = 122.2 ccs. of synthesis gas).

i.e. = 13.52 litres (at normal atmos.press).

Therefore, under pressure of 5.6 atms. the volume

= $\frac{13.52}{5.6}$ litres

= 2148 ccs.

Therefore, rate of flow over catalyst

= $\frac{2418}{16}$ = 151 ccs./min.

This rate is a function of the actual linear velocity over the catalyst/

TABLE I.

TABLE 1.

Catalyst - Ni - ThO_2. IB

Cat. Volume:- 20 ccs. (14 gms.)

Expt. No.	Temp. °C.	Synth. Gas % Found CO_2	Synth. Gas % Found H_2	Synth. Gas % Calculated. CO_2	Synth. Gas % Calculated. H_2	Gas Passed @ 1 atm. Litres.	Flow-f(V) (under press.)	Time mins.	Press. atm.	Product Gas % CO_2	Product Gas % O_2	Product Gas % CO	Product Gas % CH_4	Product Gas % H_2	Product Gas % N_2	Yield
1	300	6.0	-	5.5	90.5	17.82	107.00	20	10	1.4	0.5	-	5.25	87.0	5.8	2.34
2	290	57.1	-	57.0	39.5	18.65	80.00	30	10	67.5	0.6	-	8.5	18.6	4.8	2.64
3	270	64.0	-	64.0	32.0	27.80	107.00	30	10	70.0	0.8	-	4.1	20.5	4.5	1.89
4	282	36.0	58.3	43.2	53.0	4.93	40.80	20	10	55.1	0.4	0.5	16.5	21.6	5.9	2.0
5	293	57.0	38.0	58.1	37.4	5.43	41.70	20	10	75.4	0.5	0.4	13.5	3.3	6.9	1.83
6	298	55.0	41.0	55.0	40.0	13.85	89.00	20	10	62.0	0.4	0.4	8.7	23.8	4.7	3.01

catalyst particles and may be represented as:-

$$f(V) = 151$$

The total CH_4 formed = 5.6 % of 11.075 litres

= 628 ccs.

Therefore, (yield), ccs. CH_4 formed/cc.cat./min.

or

$$\text{ccs. } CO_2 \text{ converted/cc.cat./min.} = \frac{628}{20 \times 16} = 1.96$$

The above method of calculation was used for all experiments. Table I shows that no consistent synthesis gas compositions could be obtained in the preliminary runs. Furthermore, no water trap had been originally included in the system following the reaction chamber, and the outlet valve was being choked with condensed water resulting in irregular rate of flow and sometimes even complete stoppage. Prior to subsequent experiments therefore, the water trap was included. It was first filled with $CaCl_2$, but it was found unsatisfactory, since the $CaCl_2$ became saturated after only two runs and choked the outlet pipe. The $CaCl_2$ was therefore substituted by freshly dehydrated silica gel, which has a larger dehydrating capacity and which will not clog the passages even when supersaturated with moisture. The silica gel used was sufficient for about four runs after which it had/

had to be replaced. Each catalyst batch was also changed after 4-5 runs and freshly reduced. After each test the residual gases in the system were flushed out with hydrogen and the catalyst kept in an atmosphere of hydrogen till the next run.

Several experiments had to be rejected because of (a) sharp temperature fluctuations, (b) irregular rate of flow, (c) leaks in the outlet valve, and (d) choking of inlet pipe to reaction chamber.

During the course of a run it was sometimes found necessary to adjust the furnace rheostat. The reaction is highly exothermic and has a high temperature coefficient. It was observed that whenever there was slight overheating the effect was cumulative, and the temperature rapidly rose to a high value, sometimes as high as 450°C.

Irregular rate of flow during the course of a run was generally caused by excess moisture accumulating in the outlet valve.

In one set of experiments it was found that the yields were much lower than what was expected. On subsequent testing it was found that the inlet pipe to the reaction chamber had been choked with moist dust. The dust must have arisen from the pumice used. The moisture must have accumulated when the gases after a run were released backwards via the L.P. block.

****

CHAPTER III.

EXPERIMENTAL RESULTS AND DISCUSSION.

From Experiment 9 (Table II) onwards it was decided to dispense altogether with the circulating and storage system. Even after a number of trials, satisfactory mixing was not found possible, and what was worse, due to leaks, the composition of the stored gas was found to alter with time.

It was finally decided to try mixing by mere diffusion in a leak-proof enclosure. One of the hydrogen supply cylinders was the alternative choice for the purpose. Accordingly, carbon dioxide was fed into the cylinder via the feed block and hydrogen (from the spare cylinder) was fed in directly. At the same time the feed block was kept in communication with the regulator gauge on the H.P. block. This gauge was found to be more accurate and reliable than the other main gauges in the plant and was always used to measure the pressures of the two gases fed into the mixing cylinder.

Gases under pressure do not mix readily and it was found that if carbon dioxide was introduced first followed by hydrogen (50:50), even after 36 hours, a mixture containing 90-95 per cent. hydrogen could be tapped off. If, however, the lighter gas, hydrogen, was introduced first, followed by the much heavier carbon dioxide, complete mixing occurred on leaving/

TABLE II.

TABLE II

Catalyst - Ni - ThO_2 - IB.

Cat. Volume - 20 ccs. (14 gms.)

Expt. No.	Temp. °C.	Time mins.	Product Gas @ 1 atm. Litres.	Equivlt. Synth. Gas @ 1 atm. Litres.	f(V)	Reaction Press atm.	Synth. Gas Partial Press. CO_2 atm.	Synth. Gas Partial Press. H_2 atm.	Yield.	f(Re)
7	280	18	23.00	28.20	156.0	10.00	1.40	8.60	3.58	
8	300	18	21.50	29.20	648.0	2.50	0.59	1.91	5.36	
9	290	10	18.60	27.70	277.0	10.00	2.80	7.10	11.40	99.8
10	290	12	7.34	9.50	79.0	10.00	2.90	7.10	2.22	28.4
11	285	12	17.00	19.10	159.0	10.00	2.80	7.20	3.60	57.2
12	290	10	16.40	18.10	239.0	7.57	2.80	4.77	3.10	76.5
13	285	16	12.25	14.00	114.5	7.57	2.80	4.77	1.32	36.6
14	290	12	13.9	18.60	221.0	7.57	2.90	4.67	2.84	70.8
15	290	10	17.9	22.20	396.5	5.60	2.80	2.80	5.58	105.0
16	290	16	11.1	13.50	151.0	5.60	2.80	2.80	1.96	40.0
17	290	10	15.3	16.5	200.0	5.60	2.80	2.80	2.60	53.0
18	290	12	17.9	21.8	181.5	10.00	5.00	5.00	4.36	86.0
19	290	15	24.42	30.75	205.0	10.00	2.82	7.1	5.18	73.8 (Check Run)

TABLE II A.

TABLE IIA.

Catalyst - Ni - ThO_2 - IB.

Cat. Volume - 20 ccs. (14 gms.)

Expt. No.	Temp. °C.	f(V)	Synth.Gas. %		Product Gas %					Yield.
			CO_2	H_2	CO_2	O_2	CO	CH_4	H_2	
7	280	156	13.1	81.6	10.5	0.4	0.4	5.6	77.6	3.58
8	300	648	22.6	73.4	21.8	0.4	0.4	9.0	64.0	5.36
9	290	277	28.3	71.0	28.5	0.4	1.4	12.2	56.6	11.40
10	290	79	29.0	71.0	28.3	0.4	0.4	7.3	62.8	2.22
11	285	159	27.4	71.2	27.6	0.5	0.4	3.0	67.6	3.60
12	290	239	36.0	62.0	37.2	0.3	0.7	2.6	58.5	3.10
13	285	114.5	35.7	62.8	37.3	0.9	0.8	3.5	57.8	1.32
14	290	221	34.9	64.2	38.2	0.5	0.7	8.4	52.5	2.84
15	290	396.5	51.2	48.8	55.6	0.3	2.5	6.3	36.0	5.58
16	290	151	49.6	50.0	54.2	0.4	0.8	5.7	38.6	1.96
17	290	200	50.7	49.0	51.7	0.4	1.2	1.8	45.4	2.60
18	290	181.5	50.5	49.6	54.2	0.6	1.5	5.9	37.1	4.36
19	290	205	28.3	71.3	28.3	0.4	0.8	6.34	63.7	5.18 (Check Run.)

TABLE III.

TABLE III.

Catalyst - Ni - ThO_2 - IB.

Cat. Volume - 20 ccs. (14 gms.)

Expt. No.	Temp. °C.	Time mins.	Product Gas at 1 atm.p. Litres.	Equivlt. Synth.Gas at 1 atm. Litres.	f(V)	Reaction Press. atm.	Synth. Gas Partial Press. CO_2 atm.	Synth. Gas Partial Press. H_2 atm.	Yield.	f(Re)
20	290	14	9.48	11.80	95.7	8.80	2.70	6.10	2.06	32.2
21	290	20	13.83	16.60	93.8	8.84	2.77	6.06	1.91	31.9
22	290	15	20.96	24.15	182.0	8.84	2.74	6.02	2.62	61.8
23	295	15	29.14	32.85	248.0	8.83	2.77	6.06	3.05	84.4
24	290	20	18.80	21.92	76.0	14.60	2.90	11.60	1.88	31.9
25	290	15	29.34	33.02	152.0	14.60	2.83	11.70	3.08	63.5
26	290	15	48.60	54.00	250.0	14.40	2.90	11.50	4.30	105.0
27	290 (Check Run).	25	33.15	38.30	200.0	7.62	2.70	4.80	2.59	64.0

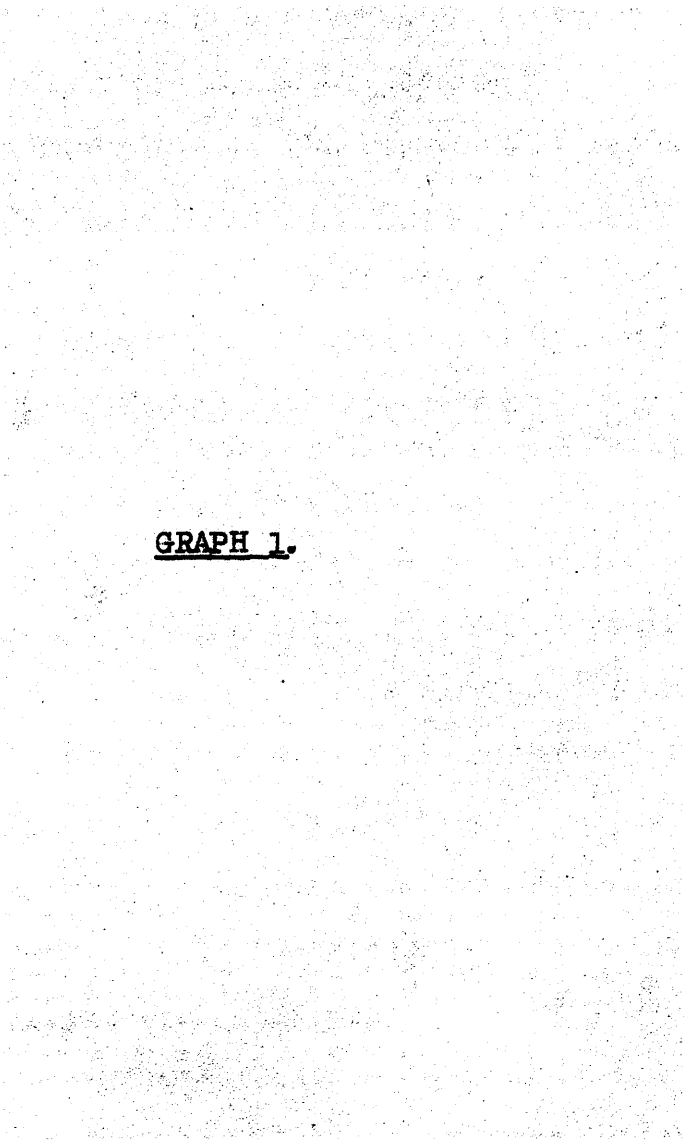
TABLE III A.

TABLE IIIA.

Catalyst - Ni - ThO_2 - IB.

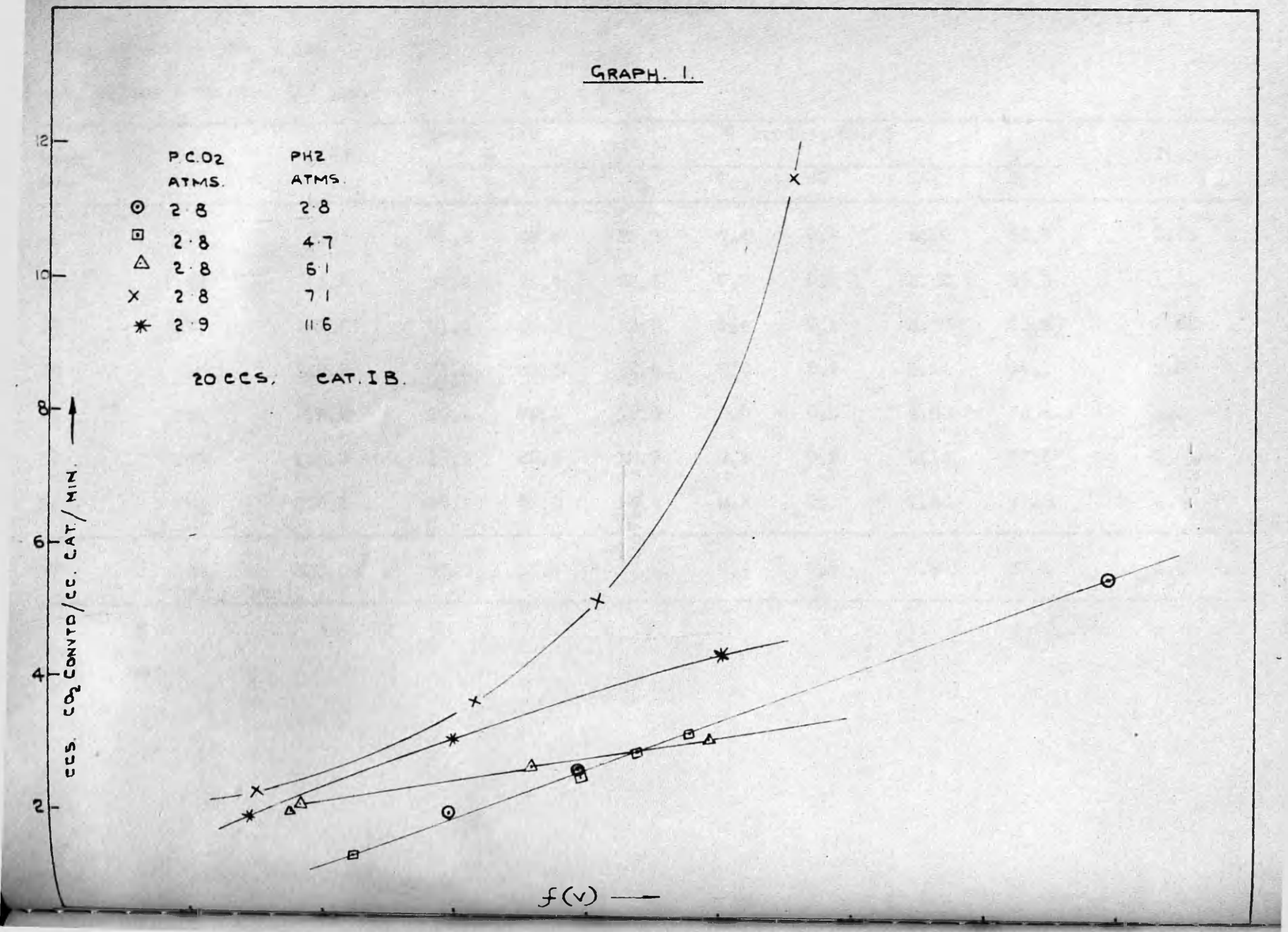
Cat. volume - 20 ccs. (14 gms.)

Expt. No.	Temp. °C.	f(V)	Synth. Gas %		Product Gas %					Yield
			CO_2	H_2	CO_2	O_2	CO	CH_4	H_2	
20	290	95.7	30.8	68.4	32.2	0.4	0.2	6.10	60.8	2.06
21	290	93.8	31.4	68.6	32.4	0.3	0.2	5.52	60.3	1.91
22	290	182.0	31.0	68.1	32.0	0.4	0.1	3.75	63.5	2.62
23	285	248.0	31.2	68.3	32.0	0.4	0.2	3.14	64.1	3.05
24	290	76.0	20.4	79.5	19.8	0.0	0.2	4.0	76.4	1.88
25	290	152.0	19.4	80.3	18.7	0.2	0.2	3.15	77.2	3.08
26	290	250.0	20.1	79.4	19.4	0.3	0.1	2.65	77.3	4.30
27	290 (Check Run).	200.0	35.5	63.0	37.1	0.6	0.2	3.90	57.2	2.59



GRAPH 1.

GRAPH. 1.


P.C.O2 ATMS.
PH2 ATMS.
2·8 2·8
2·8 4·7
2·8 6·1
2·8 7·1
2·9 11·6
20 CCS. CAT. I B.
CCS. CO2 CONVTD/CC. CAT./MIN.
f(v)
2
4
6
8
10
12

leaving overnight. (It is interesting to note that on certain occasions when the pressure was low in the carbon dioxide cylinder and it had to be fed in first, all that was necessary was to detach the mixing cylinder and leave it overnight upside down). This method of mixing was entirely satisfactory and required compositions could be obtained to ± 2 per cent. Other experimental technique of the exploratory period was found satisfactory.

In discussing the results, the effect of rate of flow will be first considered followed by the effect of varying the partial pressure of either reactant.

Effect of Rate of Flow.

Tables II, IIA, III, IIIA give the results obtained at varying rates of flow when the partial pressure of carbon dioxide was kept constant at 2.8 atmospheres and that of hydrogen varied from 2.8 - 11.6 atmospheres. These are summarised in Graph 1 of this series. The rate of reaction expressed as yield of product per unit time per unit volume of catalyst, increased with increasing linear velocity of the gases over the catalyst bed. Excepting the case when pH_2 = 7.1 atms., Graph 1 shows that the increase is gradual and almost linear within the range studied. In the case of pH_2 = 7.1 atms., the increase in yield with increasing velocity of flow is very much higher/

higher in comparison to the others.

It is known that in cases where a reaction is retarded by the products, a relatively greater increase in yield is to be expected with space velocity than in cases where the reaction is not so retarded. Burford and Frazer (108) found that water vapour is a poison for nickel hydrogenation catalysts, the effect being noticeable in their experiments at as low as 3×10^{-4} mm. pressure of vapour. The poisoning was however reversible, the catalyst being reactivated by heating in hydrogen. From their investigations on exchange reactions between deuterium and methane, Taylor and his co-workers (109) concluded that activated adsorption of methane could occur on nickel surfaces. Nicholai and others (58) found in their static experiments on the reduction of carbon dioxide, that when the products of the reaction, methane and water, were introduced in successively increasing amounts, the reaction was progressively retarded.

It thus seems very likely that the steep rise in the curve for pH_2 = 7.1 atms. is the effect of rapid removal of retarding products. In this respect the curve stands out above the others because it is here that the reaction rate is at its highest. That being so, the beneficial effect of increasing rates of flow will be most noticeable in this case. It must be admitted, however, that the experimental evidence is not sufficient for much emphasis to be laid on this effect.

In/

In these experiments also an attempt was made to correlate reaction rates with a function of the Reynolds number (Re) of the system under varying conditions. The purpose of introducing this factor may be further amplified here. A flow system is characterised by its Reynolds number which in turn characterises the laminar film produced when a fluid is flowing over solid surfaces. Theories on heat transfer indicate that the thickness of such a film in turbulent flow is inversely proportional to some power of the Reynolds number of the system, the power differing for different conditions. The film thickness should decrease as (Re) is increased, and in a reaction, if diffusion of the reactants through such a film is the controlling factor, then the rate of reaction should increase as the characteristic value (Re) increases. Whatever the absolute rates of reaction shown by differing compositions may be, the degree of increase of reaction rate with increase in (Re) should be the same for each case. In other words, when the reaction rate is plotted against (Re) the slopes of the graphs should be the same.

The Reynolds number for the experiments described here were calculated as before as a function of the actual number. The f (Re) is thus expressed as

$$\frac{f(\rho) \times f(V)}{f(\mu)}$$ (D being constant for all experiments).

f(V) was calculated as already shown in the sample calculation.

f (ρ)/

f (ρ), or a function of the average density of the gas mixtures under pressure, was calculated by multiplying the average density of the mixtures at one atmosphere pressure by the total pressure in atmospheres under which the run was made. The following density values from the International Critical Tables were used:-

H_2 - 0.8987×10^{-4} gms./cc.
CO_2 - 19.7600×10^{-4} gms./cc. at 0°C.

According to kinetic theory, the viscosity of a gas should be independent of the pressure, provided that the gas is neither (i) so rarefied that the mean free path of the molecules approach the diameter of the channel in order of magnitude, nor (ii) so dense that the molecules themselves occupy an appreciable fraction of the gas. It was therefore assumed that under the moderate pressures employed in these experiments, the viscosities of the gases were not appreciably altered and that any slight alteration was equally shared by either reactant. Accordingly, f (μ), or a function of the average viscosity was calculated from the composition after making temperature corrections for each reactant. The individual viscosities at 568°K. (295°C., i.e. 5° above recorded temperatures) were calculated according to Sutherland's formula and viscosity values from the International Critical Tables, and found to be:-

η_{568}/

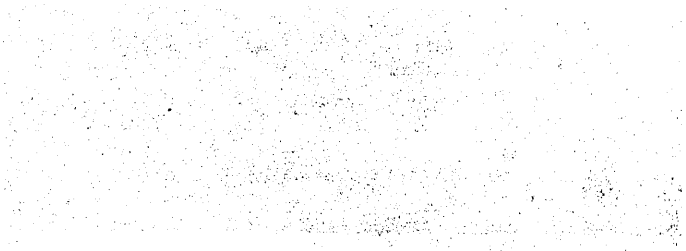
$\eta_{568}(H_2) = 136.7 \times 10^{-6}$ poises

and

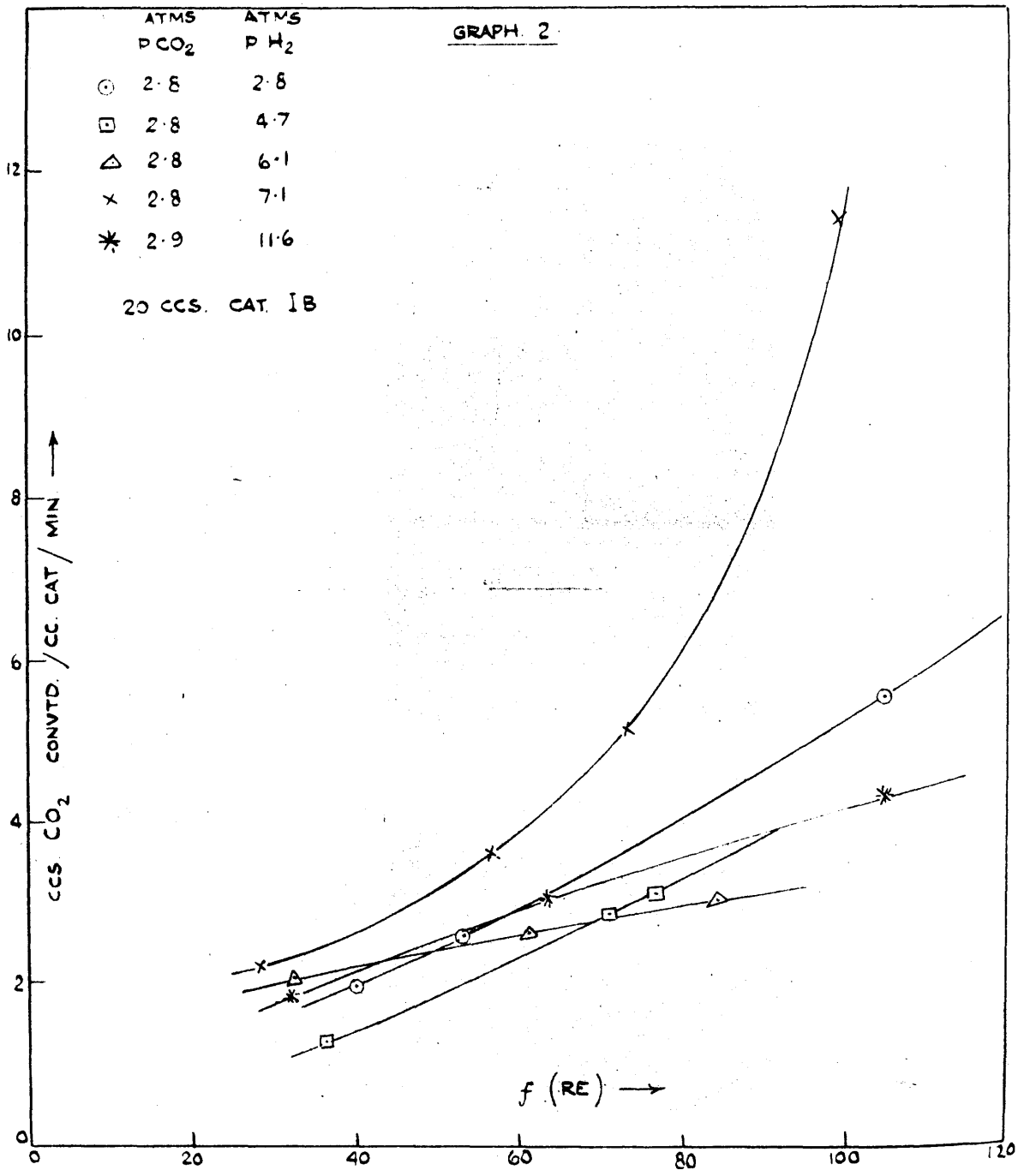
$\eta_{568}(CO_2) = 264 \times 10^{-6}$ poises.

Common multiplying factors like 10^{-4}, 10^{-6} etc., were suitably eliminated and the values of f (Re) for each experiment have been recorded in the tables.

In calculating these values the composition of the gas entering the catalyst bed alone was taken into consideration. The composition in the bed will be an average of the entering and leaving compositions. It would therefore seem more appropriate to calculate an average value of (Re) from the average composition. In order to examine how far the values of $f(Re)_{initial}$ differed from $f(Re)_{av}$, the following calculations were made for experiments 12 - 17, for varying rates of flow and varying compositions. The compositions leaving the bed were calculated backwards from the product gas analysis. Viscosities were calculated on the same basis as before but the density values were taken on a different basis ($H_2 = 1$), since such values for the products, CH_4, H_2O, CO, were readily available.



GRAPH 2.

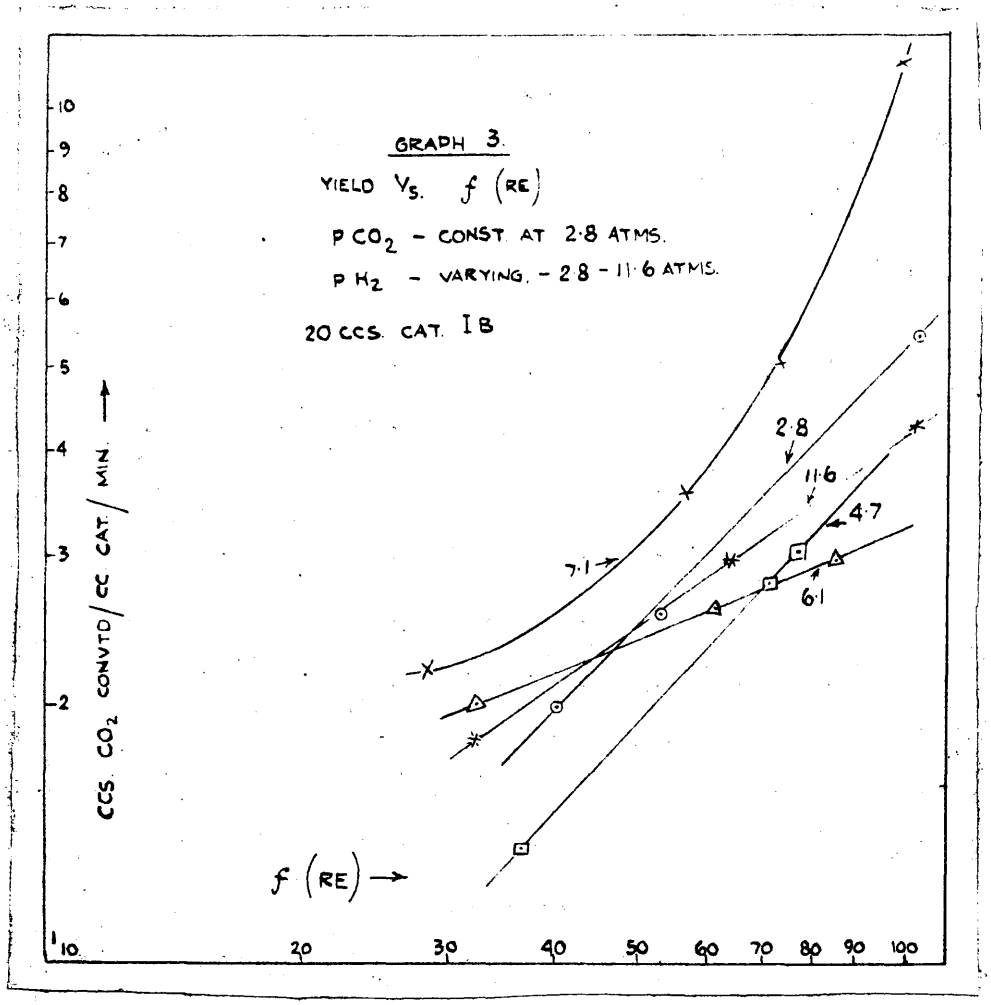

GRAPH. 2
ATMS P CO2
ATMS P H2
2·8 2·8
2·8 4·7
2·8 6·1
2·8 7·1
2·9 11·6
20 CCS. CAT. IB
CCS. CO2 CONVTD. / CC. CAT / MIN
f (RE)
0
2
4
6
8
10
12
0
20
40
60
80
100
120

Exp. No.	Initial Composition % CO_2	Initial Composition % H_2	Leaving Composition % CO_2	Leaving Composition % CO	Leaving Composition % H_2	Leaving Composition % CH_4	Leaving Composition % H_2O	Leaving Composition % $N_2 + O_2$	$f\left(\frac{\rho}{\mu}\right)$ initial	$f\left(\frac{\rho}{\mu}\right)$ average
12			35.4	0.6	55.6	2.5	4.9	1.0		46.4
13	approx. 36.0	62.0	35.5	0.6	54.0	3.3	6.5	-	46.5	47.8
14			33.2	0.3	44.8	7.2	14.3	0.2		48.4
15	approx.		49.5	2.0	31.8	5.6	11.1	-		59.3
16	50	50	48.8	0.7	34.7	5.1	10.2	0.5	57.5	58.8
17			49.6	1.2	43.6	1.7	3.4	0.5		58.0

It is seen from the above that $f\left(\frac{\rho}{\mu}\right)_{average}$ differs very little from $f\left(\frac{\rho}{\mu}\right)_{initial}$, hence it was quite reasonable to take $f\ (Re)_{initial}$ as representing the flow characteristics.

In Graph 2, the yields have been plotted against f (Re) and when compared with Graph 1 it is seen that most of the graphs intercross in a complicated way and that the graphs for pH_2 = 2.8 atms. and 4.7 atms. which formerly lay on the same line are now separated. The family of lines is essentially the same as in Graph 1. When the same relationships were plotted on a log-log paper as shown in Graph 3, the following values of the slopes were obtained:

Graph 3/



pCO_2 constant at 2.8 atms.

pH_2 (atms).	Slope
2.8	1.04
4.7	1.08
6.1	0.40
11.6	0.71

It is thus seen that no definite relationship was obtained.

Tables/

TABLE IV.

TABLE IV.

Catalyst - Ni - ThO_2 - IB.

Cat. Volume - 20 ccs. (14 gms.)

Expt. No.	Temp. °C.	Time mins.	Product Gas at 1 atm.P. litres.	Equivlt. Synth.Gas at 1 atm. litres.	f(V)	Reaction Press. atm.	Synth. Gas Partial Press. CO_2 atm.	Synth. Gas Partial Press. H_2 atm.	Yield.	f(Re)
28	285	23	13.00	16.80	90.0	8.1	5.32	2.77	2.00	44
29	290	21	26.40	31.60	186.0	8.1	5.28	2.74	3.12	91
30	290	19	49.70	58.10	376.0	8.1	5.23	2.78	5.40	184
31	285	15	22.60	25.20	165.0	10.3	6.68	3.50	2.11	102
32	290	22	17.57	19.85	88.0	10.3	7.05	3.20	1.34	56
33	290	14	21.50	23.80	164.0	10.3	7.05	3.20	2.06	104
34	290	20	31.92	34.70	168.0	10.3	7.05	3.10	1.74	107
35	290	15	34.50	37.50	244.0	10.3	7.05	3.10	2.40	155
36	290	15	21.36	22.80	127.0	12.0	9.00	2.80	1.21	100
37	285	15	36.68	40.72	230.0	12.0	9.00	2.80	1.70	181

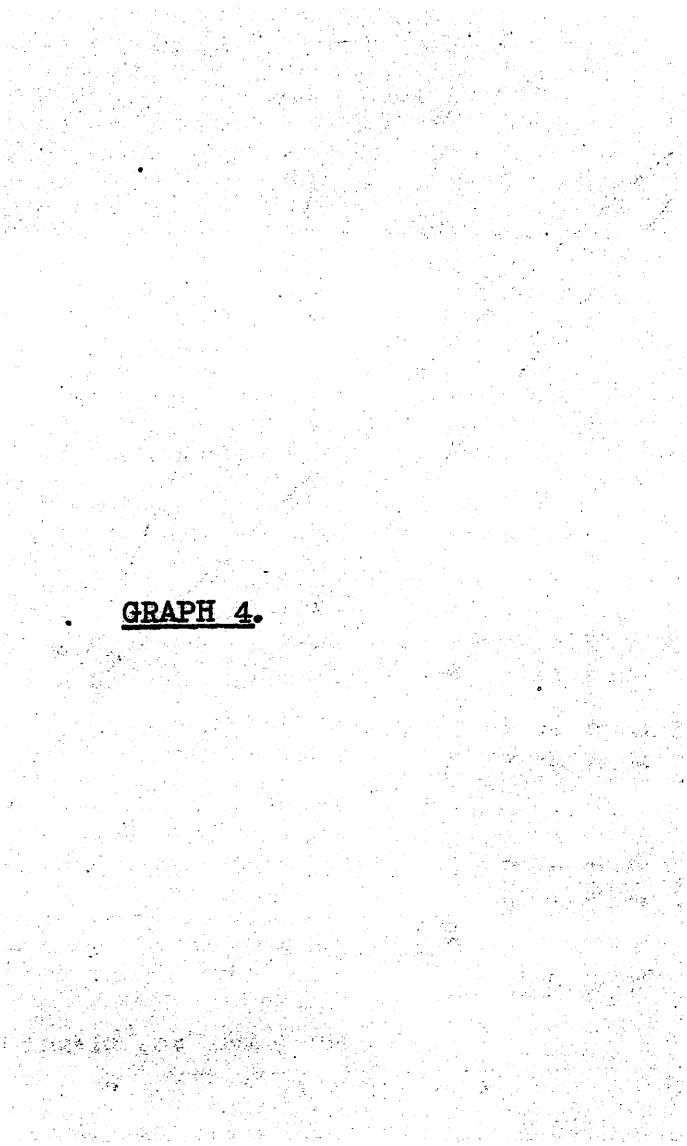
TABLE IV A.

TABLE IVA.

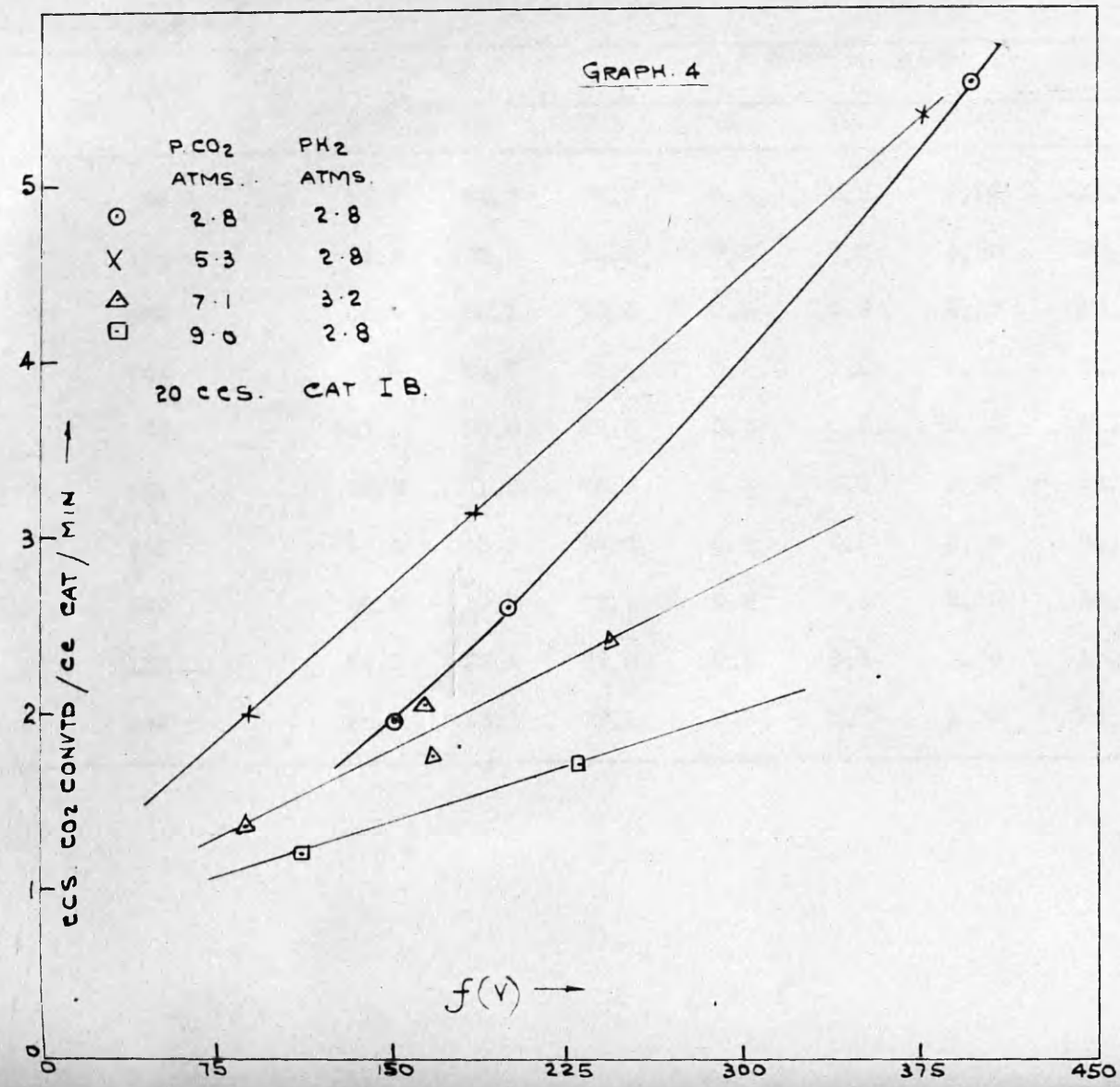
Catalyst - Ni - ThO_2 IB.

Cat. volume - 20 ccs. (14 gms.)

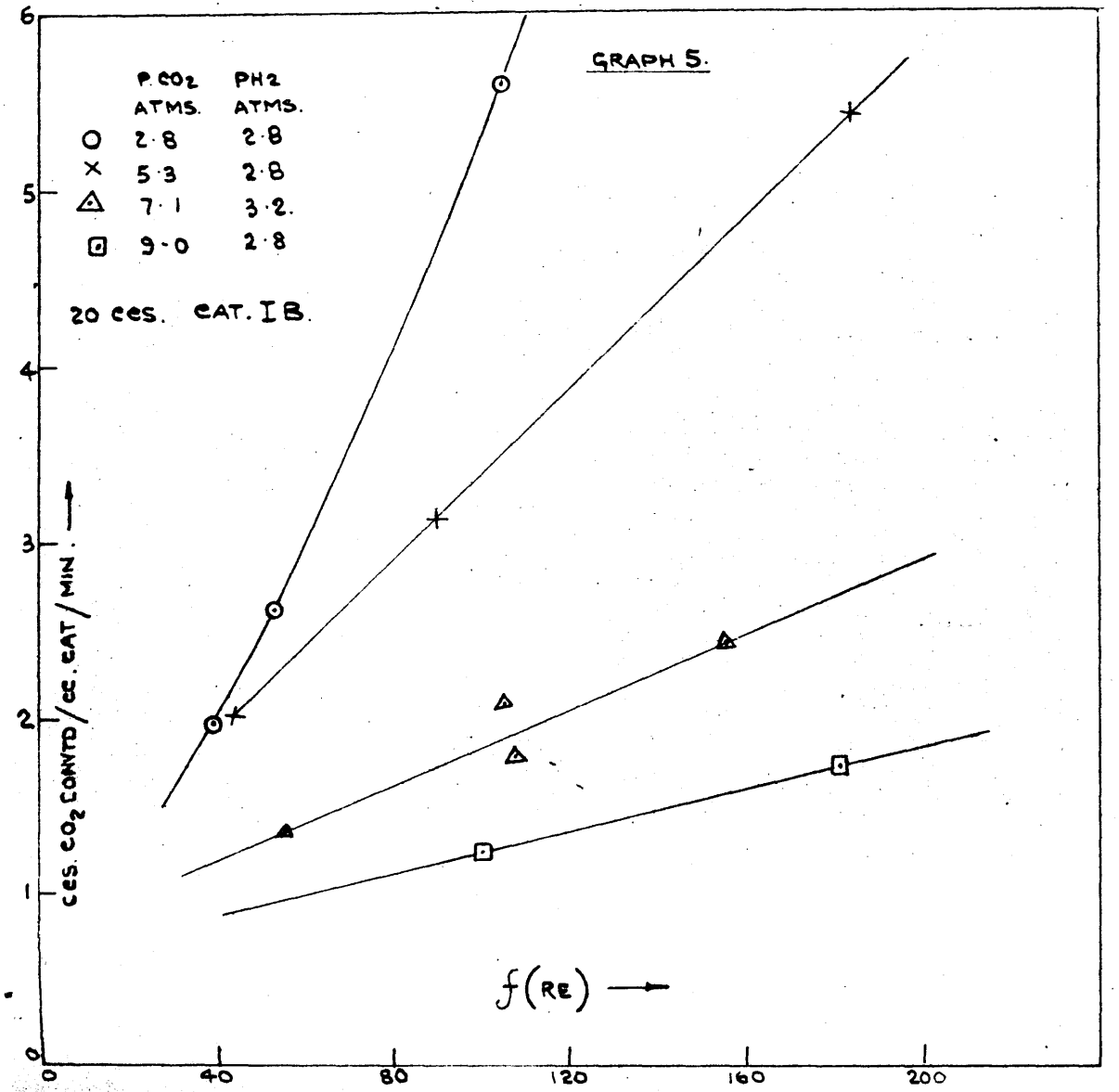
Expt. No.	Temp. °C.	f(V)	Synth.Gas %		Product Gas %					Yield.
			CO_2	H_2	CO_2	O_2	CO	CH_4	H_2	
28	285	90	65.7	34.2	77.6	0.3	0.2	7.10	15.8	2.00
29	290	186	65.2	33.8	72.3	0.3	0.8	4.95	20.6	3.12
30	290	376	64.6	34.3	70.4	0.3	0.9	4.15	23.5	5.40
31	285	165	64.8	34.0	69.0	0.6	0.2	2.80	26.6	2.11
32	290	88	68.2	30.8	73.6	0.5	0.2	3.36	21.4	1.34
33	290	164	68.5	31.0	72.5	0.4	0.2	2.68	23.4	2.06
34	290	168	68.4	30.3	72.0	0.5	0.2	2.18	24.3	1.74
35	290	244	68.5	30.8	72.3	0.5	0.3	2.10	24.8	2.40
36	290	127	76.7	23.2	79.8	0.1	0.3	1.70	18.0	1.21
37	285	230	76.7	23.1	79.1	0.3	0.2	1.32	19.1	1.70



GRAPH 4.


GRAPH. 4
P CO2 ATMS.
PH2 ATMS.
⊙ 2·8 2·8
X 5·3 2·8
△ 7·1 3·2
⊡ 9·0 2·8
20 CCS. CAT I B.
CCS. CO2 CONVTD / CC CAT / MIN
f(V)
0
1
2
3
4
5
0
75
150
225
300
375
450

GRAPH 5.

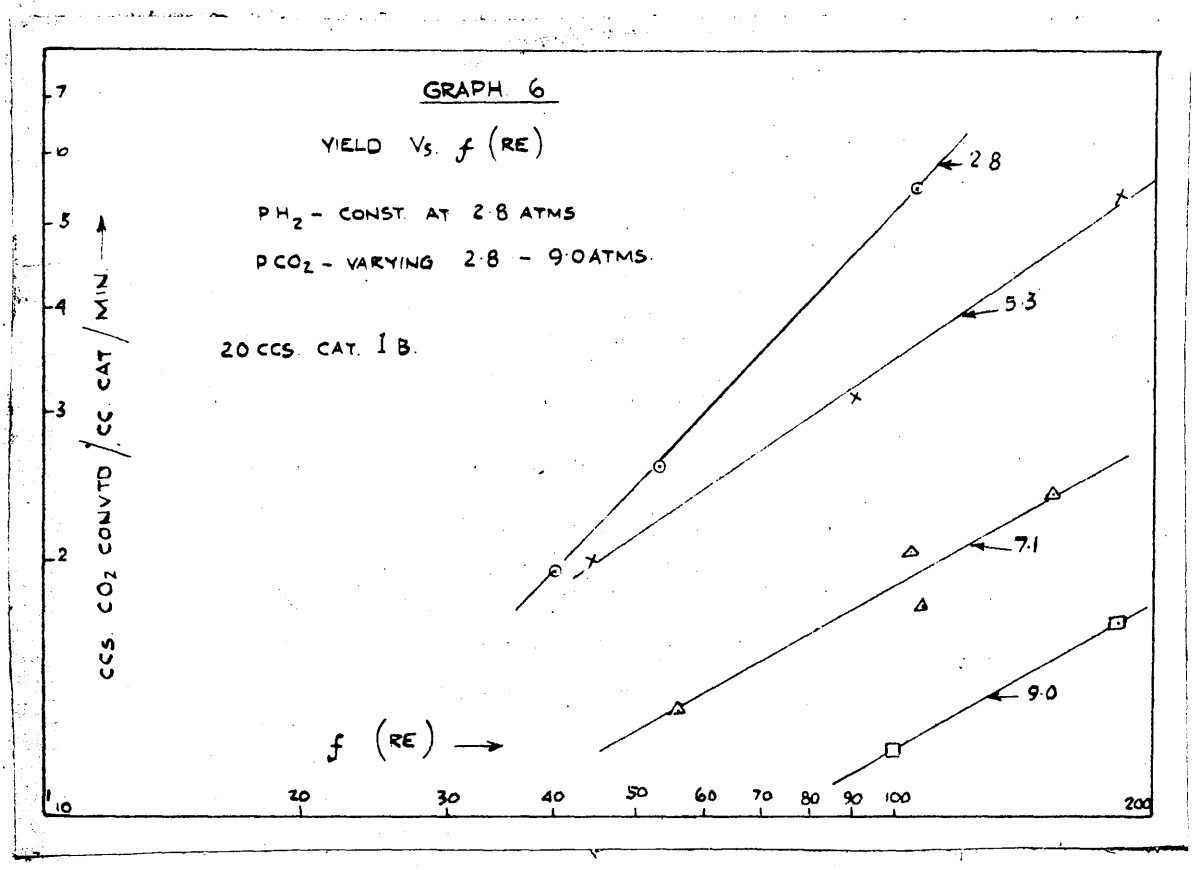

GRAPH 5.
P.CO2 ATMS.
PH2 ATMS.
2·8 2·8
5·3 2·8
7·1 3·2.
9·0 2·8
20 ces. CAT. IB.
CES. CO2 CONVTD/CC. CAT/MIN.
f(RE)
0
1
2
3
4
5
6
0
40
80
120
160
200

Tables IV and IVA give the results obtained when the partial pressure of hydrogen was kept constant at about 2.8 atms. and that of carbon dioxide varied from 2.8 - 9.0 atms. Graph 4 shows the plots of yield against f (V). The effect of plotting yields against f (Re) is shown in Graph 5. It will be noticed that whereas in Graph 4 the curve for p CO_2 = 2.8 atms. lies below that for p CO_2 = 5.3 atms., on plotting against f (Re), the positions are reversed. This lateral displacement to the right of the Graph for p CO_2 = 5.3 atms. occurs because, being at a higher pressure and with a denser composition, the values for f (Re) for the same values of f (V) are higher than when p CO_2 = 2.8 atms. In a similar way, the graphs for p CO_2 = 7.1 and p CO_2 = 9.0 atms. are also seen to be displaced to the right. When this relationship of yield versus f (Re) was plotted on a log-log paper as shown in Graph 6, the following values of the slopes were obtained:-

pH_2 = 2.8 atms.

pCO_2 (atms).	Slope.
2.8	1.04
5.3	0.687
7.1	0.568
9.0	0.586

Graph 6/



In this case also no definite relationship with f (Re) was observed, apart from the fact that the slopes from p CO_2 = 5.3 atms. onwards, are very nearly the same. This indicates that for high concentrations of carbon dioxide, the variations in yields with varying linear velocities of flow are nearly of the same order.

Some experiments were also carried out on the unpromoted nickel catalysts II, and these are recorded in Tables V and VA. Unfortunately, rather anomalous values were obtained/

TABLE V.

TABLE V.

Ni Catalyst II

Cat. volume - 20 ccs.

Expt. No.	Temp. °C.	Time mins.	Product Gas at 1 atm.p. Litres.	Equivlt. Synth.Gas at 1 atm. Litres.	f(V)	Reaction Press. atm.	Synth. Gas Partial Press. CO_2 atm.	Synth. Gas Partial Press. H_2 atm.	Yield.
38	300	28	17.6	22.5	144	5.60	2.8	2.8	2.22
39	285	18	22.6	25.1	248	5.60	2.8	2.8	1.77
40	285	30	56.4	64.4	384	5.60	2.8	2.8	3.43
41	285	30	30.6	33.8	113	10.00	5.0	5.0	1.37
42	285	28	38.3	43.5	155	10.00	5.0	5.0	2.35
43	285	15	24.4	26.8	179	10.00	5.0	5.0	2.10
44	290	20	17.8	20.1	135	7.62	2.7	4.8	1.46
45	285	15	18.9	21.8	190	7.62	2.7	4.9	2.40
46	285	12	28.8	30.9	337	7.62	2.7	4.8	2.20
47	285	15	15.5	17.3	115	10.00	2.9	7.0	1.48
48	285	15	35.3	38.2	254	10.00	3.0	6.9	2.36
49	285	9	64.7	68.3	759	10.00	3.1	6.8	4.92
50	290	15	26.2	28.5	346	5.60	1.7	3.9	2.30

TABLE V A.

TABLE VA.

Ni Catalyst. II

Cat. volume - 20 ccs.

Expt. No.	Temp. °C.	f(V)	Synth. Gas %		Product Gas %					Yield.
			CO_2	H_2	CO_2	O_2	CO	CH_4	H_2	
38	300	144	48.7	49.2	55.0	0.6	0.5	7.10	34.8	2.22
39	285	248	49.0	49.2	51.3	0.4	0.4	2.80	43.6	1.77
40	285	384	47.7	49.0	50.5	0.7	0.5	3.66	41.5	3.43
41	285	113	48.7	49.2	50.8	0.5	0.5	2.70	43.7	1.37
42	285	155	48.2	49.3	51.2	0.2	0.2	3.50	42.4	2.35
43	285	179	48.2	49.3	50.2	0.5	0.4	2.60	44.1	2.10
44	290	135	35.8	62.4	37.0	0.8	0.2	3.30	57.4	1.46
45	285	190	35.2	64.8	36.5	0.7	0.4	3.70	59.7	2.40
46	285	337	35.2	63.1	35.8	0.8	0.2	1.80	60.5	2.20
47	285	115	28.7	69.5	38.9	0.7	0.2	2.86	65.9	1.48
48	285	254	30.1	68.5	30.4	0.8	0.1	2.00	65.9	2.36
49	285	759	31.1	67.7	31.0	0.1	0.5	1.37	65.9	4.92
50	290	346	29.6	69.0	29.6	0.4	0.5	2.70	65.5	2.30

obtained and the results have not been plotted. No confirmation of the results was possible because the outlet valve failed repeatedly even after repeated repairs and two replacements.

Effect of varying the partial pressure of either reactant.

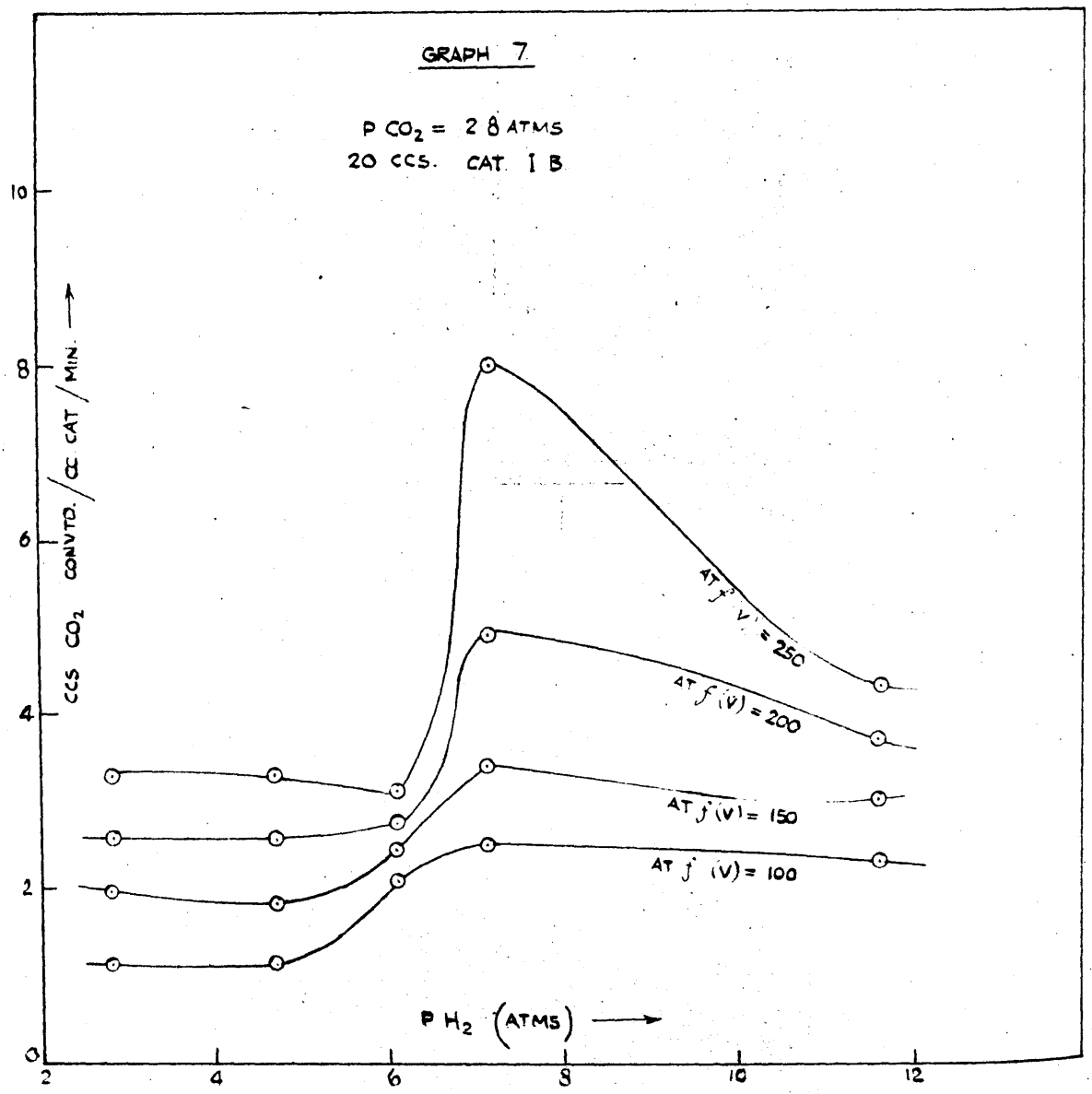
When the partial pressure of carbon dioxide was kept constant at 2.8 atms. and that of hydrogen varied, it will be observed from Graph 1 that the reaction rate at first remained constant. On further increase in hydrogen pressure the rate rose to a high value and then decreased. At pH_2 = 7.1 atms. the reaction rate was at its highest and this increase was very much accentuated with increasing rate of flow. Table VI has been drawn up from Graph 1.

TABLE VI

pCO_2 atms.	pH_2 atms.	Yield at f (V) = 100	150	200	250
2.8	2.8	1.10	1.95	2.60	3.30
2.8	4.7	1.10	1.82	2.60	3.30
2.8	6.1	2.10	2.42	2.75	3.06
2.8	7.1	2.50	3.40	4.90	8.00
2.9	11.6	2.30	3.00	3.70	4.30

These/

GRAPH 7.


GRAPH 7
P CO2 = 2.8 ATMS
20 CCS. CAT. I B
CCS CO2 CONVTD. / CC CAT / MIN. ⟶
P H2 (ATMS) ⟶
AT f(V) = 250
AT f(V) = 200
AT f(V) = 150
AT f(V) = 100
0
2
4
6
8
10
12

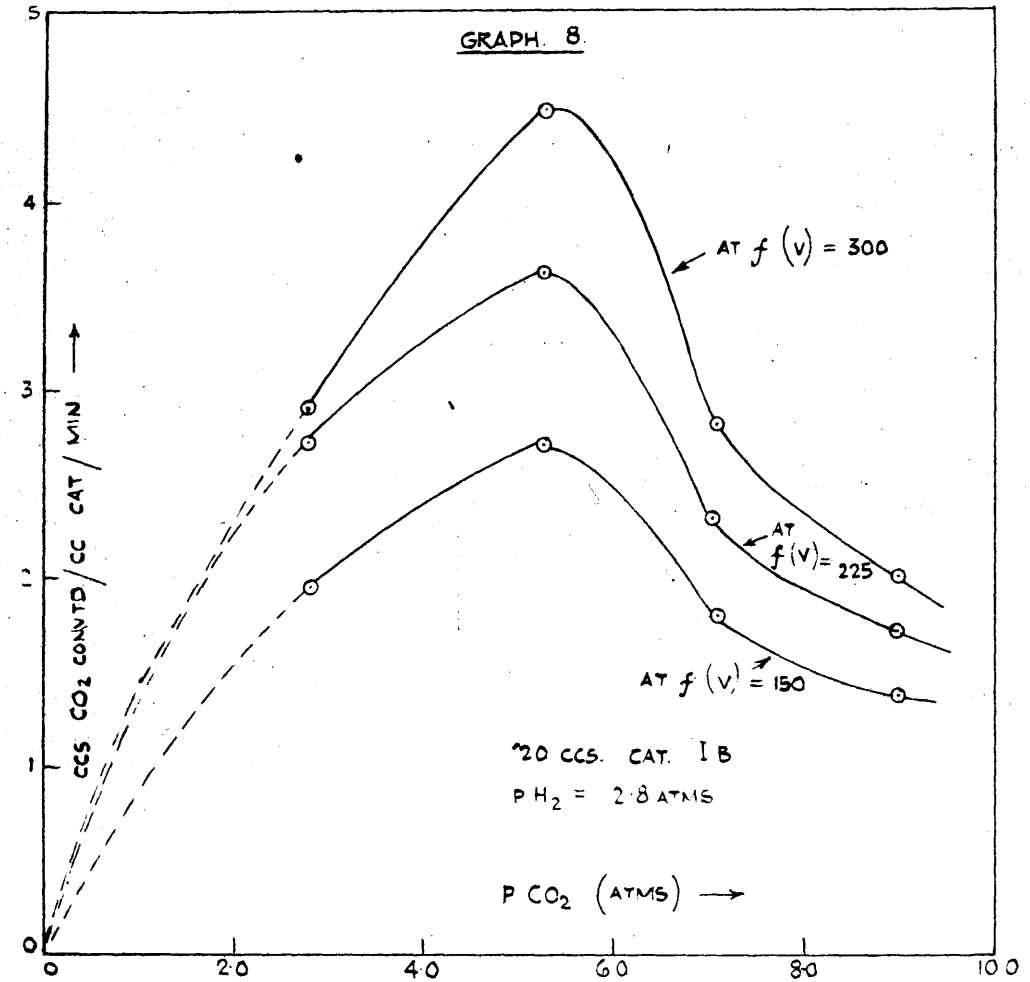
These values when plotted in Graph 7 show clearly the variations in yield with varying pH_2 at regular flow intervals. It will be observed that the rise and fall in the curves are accentuated as the flow is increased. The very high reaction rate at p CO_2 = 2.8 atms. and p H_2 = 7.1 atms. would indicate that under such conditions an ideal concentration of the reactants is produced on the catalyst surface. It is not quite clear as to why the rise in the curves should be preceded by a portion indicating constant yield. It may mean that initially, the carbon dioxide being more strongly adsorbed than hydrogen, is not easily dislodged, such a process being essential for maximum reaction rate.

If the results of Graph 4 are analysed in a similar way, it will be noted that on keeping pH_2 constant at 2.8 atms. (in one case pH_2 rose to 3.2 atms.) and on raising the pressure of carbon dioxide, the yield rises at first and then falls rapidly. This is brought out clearly by Table VII and the corresponding Graph 8.

TABLE VII

pCO_2 atms.	pH_2 atms.	Yield at f (V) = 150	225	300
2.8	2.8	1.95	2.91	4.0
5.3	2.8	2.70	3.60	4.48
7.1	3.2	1.80	2.30	2.80
9.0	2.8	1.38	1.70	2.00

GRAPH 8.


GRAPH. 8.
CCS CO_2 CONSTD / CC CAT / MIN ⟶
AT $f(v) = 300$
AT $f(v) = 225$
AT $f(v) = 150$
20 CCS. CAT. I B
$P H_2 = 2.8$ ATMS
$P CO_2$ (ATMS) ⟶
0
1
3
4
5
2·0
4·0
6·0
8·0
10·0

GRAPH 9.

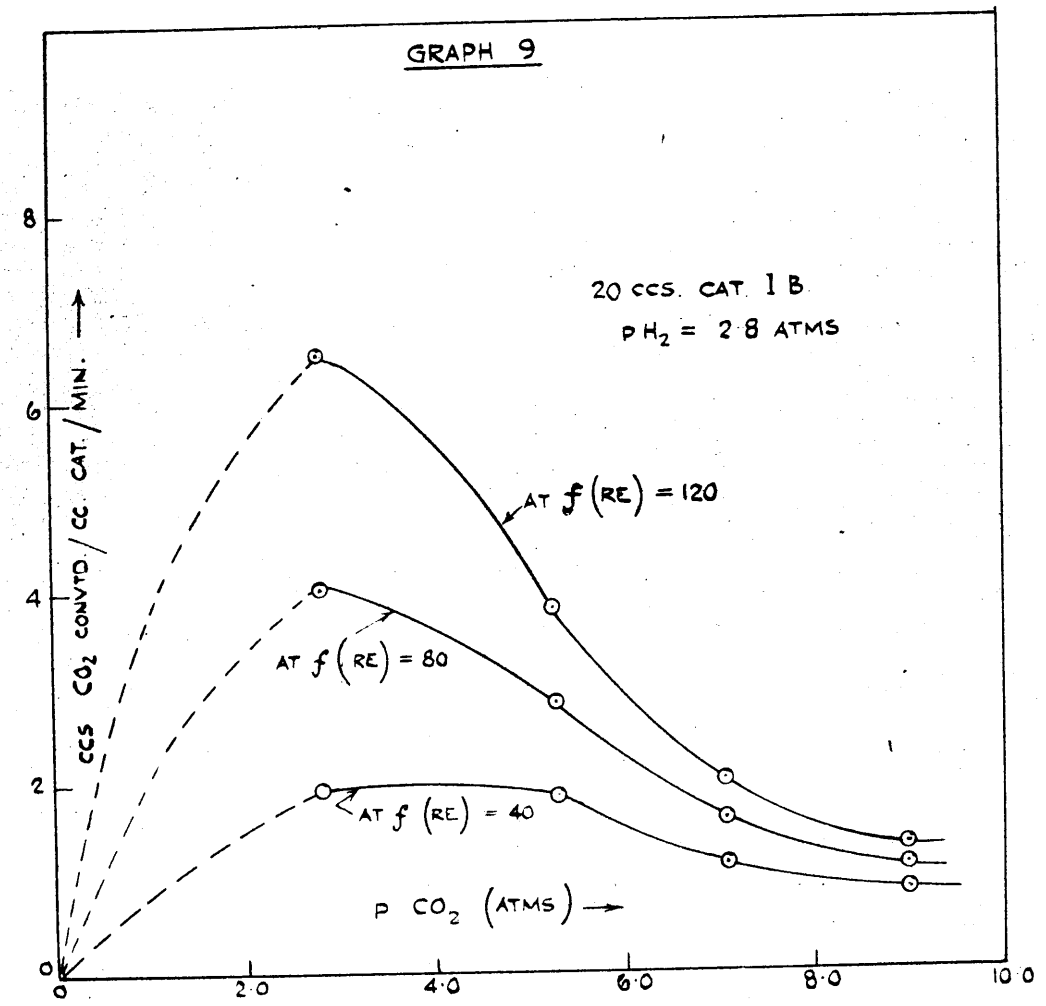

GRAPH 9
20 ccs. CAT. 1 B
P H2 = 2·8 ATMS
AT f (RE) = 120
AT f (RE) = 80
AT f (RE) = 40
ccs CO2 CONVTD / cc. CAT. / MIN.
P CO2 (ATMS)
0
2·0
4·0
6·0
8·0
10·0
2
4
6
8

Table VIII and the corresponding Graph 9 show the change produced on plotting yields against increasing p CO_2 at various values of f (Re). The peaks in the curves are shifted to the left.

TABLE VIII.

pCO_2 atms.	pH_2 atms.	Yield at f (Re) = 40	80	120
2.8	2.8	1.96	4.04	6.5
5.3	2.8	1.90	2.87	3.82
7.1	3.2	1.17	1.60	2.02
9.0	2.8	0.85	1.10	1.32

Hinshelwood (110) has observed that every such experimental study "made under conditions circumscribed by the limitations of practical technique reveals only a fragment of the complete set of relations." In the experiments described here one of these limitations is the effect of total pressure. The reaction is accompanied by diminution in volume and therefore increase in pressure is likely to have had an effect. This effect would however be small because the equilibrium is already far to the right.

A comparison may now be made between the results obtained in/

in Parts I and II of the experimental section with those obtained by Nicolai and others.(58) Strictly speaking, such a comparison is not justifiable because the results obtained by Nicolai et al are for quite different conditions. They worked under static conditions and under pressures below atmospheric, whereas the experiments that have been described so far were conducted under streaming conditions and at atmospheric pressure and above. However, the comparison has been recorded as of interest.

The reaction can be expressed by the general expression which connects reaction between two bodies:- $V = K.\theta H_2.\theta CO_2$, where θ represents fraction of the surface covered by the reactants. Then if 'b' is the coefficient of adsorption, the expression is:-

$$V = K \cdot \frac{b\,H_2 \cdot pH_2}{1 + bH_2\,pH_2 + bCO_2\,p\,CO_2} \times \frac{b\,CO_2 \cdot pCO_2}{1 + bH_2\,pH_2 + bCO_2\,pCO_2}$$

An analysis of this expression shows that for a given pressure of one of the reactants, the velocity of reaction varies as a function of the pressure of the other to reach a maximum and then to diminish. With a catalyst active at a low temperature, Nicolai et al (loc.cit.) obtained the curves shown in Figure 15 , where the partial pressure of hydrogen was kept constant and that of carbon dioxide varied. They show a rise followed by a fall in reaction velocity. These may be roughly compared with Graphs 7 and 8 of the present series of experiments.

Figure __/

FIGURES 16 AND 17.

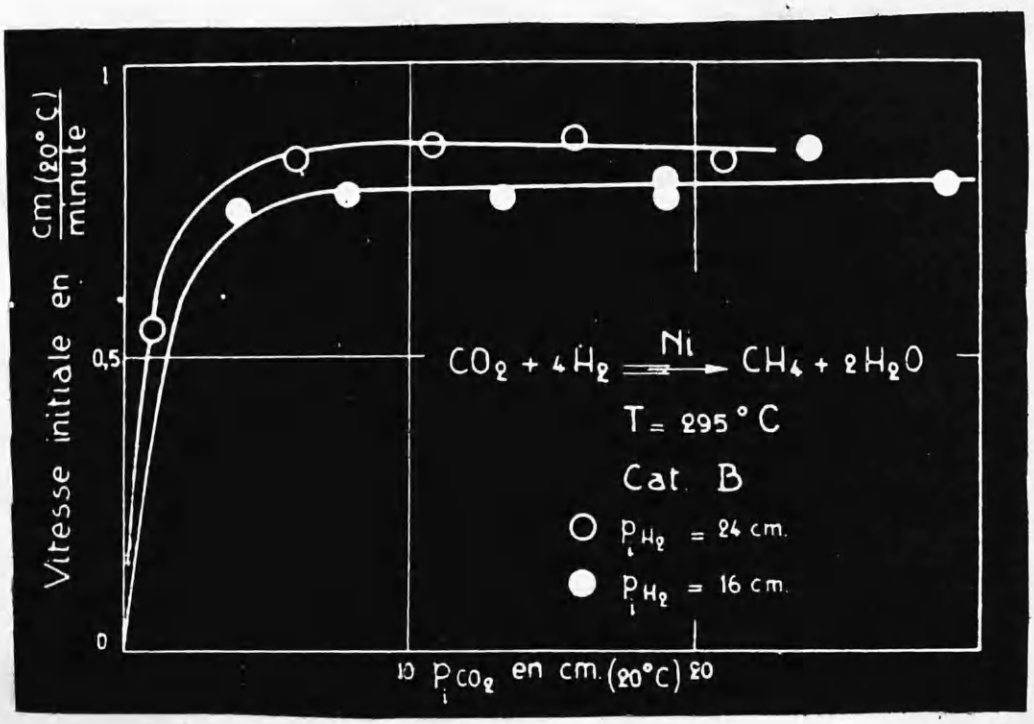


FIGURE 16.

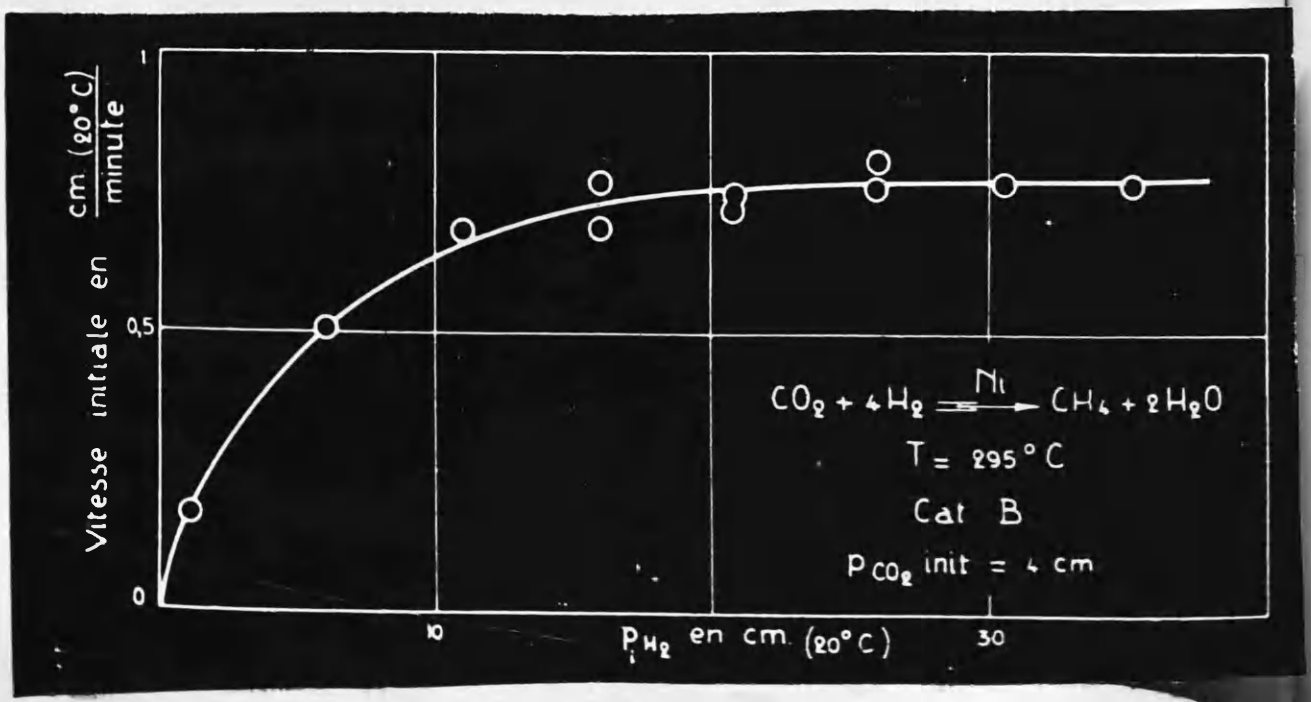


FIGURE 17.

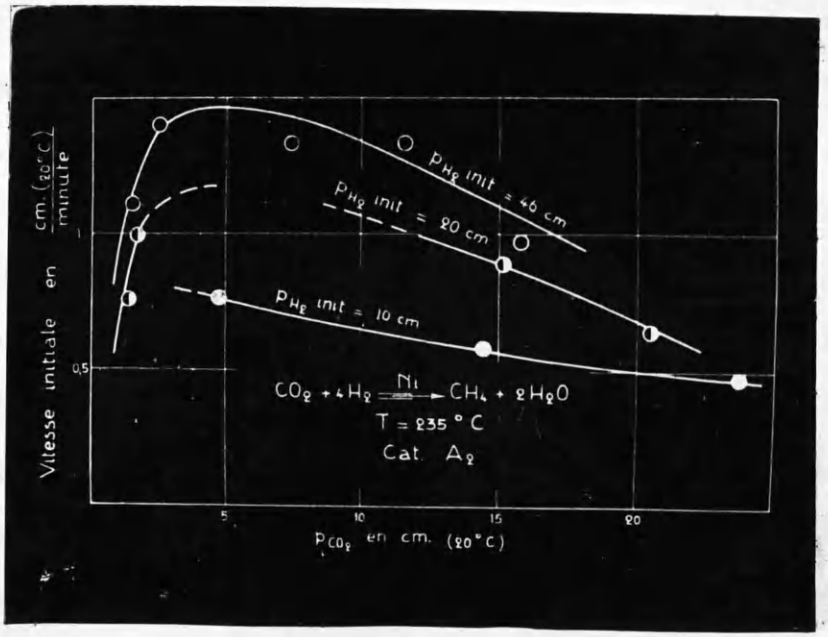


Figure 15.

With a catalyst active at a higher temperature, however, they obtained curves shown in Figures 16 and 17 . In this case, the reaction velocities reached a constant value as the partial pressure of either reactant was varied with respect to the other. Figure 16 may be compared with Graph 8 of Part I (page 93) and the first half of Figure 17 may be compared with Graph 9, Part I, (page 94).

Summarising, it appears from the experimental data of Parts I and II, that both carbon dioxide and hydrogen are adsorbed on the catalyst surface and that either of these adsorptions/

adsorptions tends to check the other. Beyond certain arbitrary ratios which show maximum rate of reaction, excess pressure of either reactant checks the reaction. Since both reactants are adsorbed, this appears to be a case where the reaction is occurring between adjacently adsorbed molecules on the surface.

In accordance with the general behaviour shown by all streaming reaction systems, the rate of reaction as denoted by the space-time yield, rises with increasing rate of flow. The degree of increase is different for different compositions of reactants and in general, the degree of increase is greater when the reaction rates are higher. It appears that diffusion of reactants through a gas film on the catalyst surface is not the controlling factor in the reaction. The reaction is governed by the ratios of reactants adsorbed on the surface, and when produced in large amounts, the reaction products probably exercise a retarding influence.

Side Products.

There are two other reaction products which must be mentioned. It will be noted from the Tables for the pressure reactions that carbon monoxide was always found in the product gas. The amounts formed per minute are particularly high in the case of experiments 9, 15, 17, 18 and 30. It will be noted that in these experiments the yields of methane are also high and carbon dioxide concentrations are high too. This seems to indicate/

indicate that there is some relation between the carbon monoxide formed and the main reaction, and it appears in appreciable amounts when it can escape hydrogenation.

The used silica gel on each occasion had a faint fruity odour like that of an ester. When the silica gel was heated in a small distilling flask, the water that was driven off and collected also had the same odour. The amounts were too small for any analysis to be made.

These two products will be considered more fully in the final discussion.

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PART III.

INVESTIGATIONS INTO THE BEHAVIOUR OF POSSIBLE INTERMEDIATES IN THE INTERACTION OF CARBON DIOXIDE AND HYDROGEN.

CHAPTER I.

ATTEMPTED CARBIDE FORMATION.

Introductory.

Having found that the reaction proceeds by way of interaction between adsorbed molecules of both reactants, the next step in the reaction needed investigation.

Russell and Taylor (37) showed that carbon dioxide is appreciably absorbed by nickel and nickel-thoria catalysts at 285-345°C., and Chakraverty (117) observed the same with promoted nickel catalysts at 400-450°C. The nature of this adsorption is, however, not clear. Kawakita (111) observed remarkable chemisorption of carbon dioxide by reduced iron at 300-400°C. From experimental evidence, it was concluded that the adsorbed molecules, after diffusion into the inner surfaces of the catalyst through minute cracks and grain boundaries, acted upon the iron atoms, according to such a heterogeneous chain reactions as:-

(i) $Fe + (CO_2)_{ads.} = Fe_xO_y + (CO)_{ads.}$

(ii) $2\,(CO)_{ads.} = C + (CO_2)_{ads.}$

On further investigation, carbon monoxide was identified as an intermediate and the formation of Fe_3O_4 and free carbon was noted. (112) These facts, supported by free energy considerations, suggested that the mechanism was:-

Fe/

$$Fe + CO_2 = FeO + CO$$

$$3\ FeO + CO_2 = Fe_3O_4 + CO$$

$$3\ Fe + 4\ CO_2 = Fe_3O_4 + 4\ CO$$

$$2\ CO = C + CO_2$$

The apparent reaction of the system becomes:-

$$3\ Fe + 2\ CO_2 = Fe_3O_4 + 2C.$$

Doelemann (113) gave a somewhat similar explanation for the water gas reaction, $CO_2 + H_2 \rightarrow CO + H_2O$, on an iron catalyst at 910°C. The transfer of an oxygen atom from carbon dioxide to hydrogen through the intermediate formation of adsorbed oxygen on iron was suggested:-

$$CO_2\ (gas) \rightleftharpoons CO\ (gas) + O(ads.)$$

$$O\ (ads) + H_2(gas) \rightleftharpoons H_2O\ (gas)$$

$$C\ (\text{dissolved in } \gamma\text{-Fe}) + O(ads.) \rightleftharpoons CO\ (gas).$$

Among the several mechanisms which were suggested in the Introductory section (pages 45-6), for methane synthesis from carbon dioxide and hydrogen, mechanisms 2a and 5a postulated the intermediate formation of "surface carbide," either by the intermediate formation of carbon monoxide, or via dioxymethylene. These possibilities may be expressed in general terms as:-

(1) $CO_2 + H_2 = CO + H_2O$, followed by

(1a) $2\ CO = C + CO_2$

or

(1b) $CO + H_2 = C + H_2O$

(2) $CO_2 + 2H_2 = C + 2\ H_2O$

It/

It will be noted that all the above reactions involve the presence of hydrogen as an oxygen acceptor. In this respect, carbon dioxide is quite different from carbon monoxide; it is well known that carbon monoxide is decomposed by iron, cobalt and nickel to the respective carbides without the need for any external oxygen acceptor, in the sense of the equation:-

$$3\ Ni + 2\ CO = Ni_3C + CO_2$$

In this case one molecule of carbon monoxide acts as an oxygen acceptor for the other. This reaction was first examined by Bahr and Bahr (114), followed by Fischer and Tropsch and by Tutija. (115) It is, however, interesting to note that in their first successful attempt at methane synthesis from the oxides of carbon, Sabatier and Senderens (49) in 1902, recorded that the nickel catalyst became carbided. The decomposition of carbon monoxide by nickel catalysts has recently been studied in some detail by Tebboth, (116) who found that unsupported and unpromoted nickel catalysts showed little activity for the decomposition, whereas the addition of thoria and Kieselgurh caused a marked increase in rate of decomposition at 250-450°C. Elementary carbon formation occurred at all temperatures.

In order to detect possible carbide formation from carbon dioxide by way of equations 1, 1a, 1b and 2, it was necessary to assume:-

(a) that the rate of carbide formation is high, and

(b)/

(b) that in the absence of sufficient hydrogen on the catalyst surface, all the carbide formed will not be hydrogenated to methane.

The nickel catalyst should then be carbided on treatment with gas mixtures rich in carbon dioxide and poor in hydrogen. The carbide formed, if any, could be detected as methane on subsequent passage of hydrogen over the treated catalyst. With this end in view, the following experiments were carried out.

EXPERIMENTAL.

Carbide Formation with Carbon Monoxide.

The apparatus employed was the same as that described in Part I. It was first necessary to test whether the nickel-thoria catalyst was active in decomposing carbon monoxide and whether the carbide thus formed, could be readily hydrogenated and detected as methane.

The Ni - ThO_2 catalyst IB, (8.2 ccs., 5.60 gms.) was first reduced with hydrogen. The hydrogen in the system was flushed out very thoroughly with nitrogen and carbon monoxide was passed over the catalyst. The carbon monoxide was prepared by the action of concentrated sulphuric acid on 98 per cent. formic acid.

(1)/

(1) Temp. 290°C.

As the CO was being passed, the outgoing gas was bubbled through lime water, which was repeatedly changed. In all cases, the lime water turned turbid rapidly, showing a continuous formation of CO_2. The CO passed was 1 litre in 17 minutes. On subsequent flushing with nitrogen followed by passage of hydrogen, gas of the following composition was obtained:-

Volume	=	500 ccs.	
CO_2	-	0.0%	
O_2	-	0.3	
CO	-	0.0	
H_2	-	64.0	
CH_4	-	5.4	= 27.0 ccs.
N_2	-	30.3	
		100.0	

(2) Temp. 290°C.

CO passed - 1.5 litres in 28 minutes.

Flushed with nitrogen. Volume collected - 1.7 litres.

CO_2 in gas - 2.7 per cent., i.e. 46 ccs. CO_2 produced.

Flushed with nitrogen

H_2 then passed - 1.0 litre in 12 minutes.

Flushed with Nitrogen. Total volume collected - 1.23 litres.

Gas/

Gas composition.

CO_2 - 0.0%

O_2 - 0.1

CO - 0.0

H_2 - 66.1

CH_4 - 6.5 = 80.0 ccs.

N_2 - 27.3

100.0

The CH_4 produced should have been equal to about 46.0 ccs., on the assumption that all the carbide formed by the passage of CO would be hydrogenated on subsequent treatment with hydrogen. However, 80 ccs. of CH_4 were found. The excess might have arisen from some CO held tenaciously by the catalyst, or remaining in pockets preceding the catalyst chamber. The following hydrogen balance, made on the assumption that <u>all</u> the carbide formed was hydrogenated to CH_4 and that the excess CH_4 must have arisen from the hydrogenation of CO, shows very good agreement:-

H_2 passed - 1000 ccs.

H_2 recovered:-

As free H_2.....812 ccs.

In CH_4 formed by assuming

that 46 ccs. were produced

by the reaction $C + 2H_2 = CH_4$...92 ccs.

In rest of CH_4, assuming

formed by reaction -

$CO + 3H_2 = CH_4 + H_2O$.....102 ccs.

1006 ccs.

This/

This showed that almost all the carbide formed could be hydrogenated to methane.

(3) Same procedure as above.

Product gas (600 ccs.) on hydrogenation contained no CO_2 or CO and the CH_4 content was 5.6%, i.e. 33.6 ccs.

The catalyst was therefore fairly active in decomposing CO and the carbide thus formed, was sufficiently reactive to give methane on subsequent hydrogenation.

Attempts at carbide formation with Carbon Dioxide and Hydrogen.

The first two experiments described hereafter were carried out as blank tests, by treating the catalyst with CO_2 alone, followed by flushing with nitrogen and subsequent passage of hydrogen. The temperature was about 290°C. in all cases.

(1) and (2)

CO_2 passed - 1.5 litres in 15 mins.

Flushed with nitrogen and hydrogen passed.

Gas collected - 1.0 litre.

Analysis:-

		(1) %	(2) %
CO_2	-	0.0	0.0
O_2	-	0.3	0.4
CO	-	0.0	0.1
CH_4	-	1.0	1.0
H_2	-	83.0	84.6
N_2	-	15.7	13.9
		100.0	100.0

The/

The 1.0% CH_4 found was equivalent to a 0.1 cc. contraction only in the gas analysis apparatus and therefore unreliable.

(3) Test with mixture:- CO_2 - 90%, H_2 - 10%

Two litres passed in 20 minutes.

H_2 flushing gas - 1.0 litre.

CO_2 - 0.0%, CO - 0.0%, CH_4 - 1.8%

The excess of CH_4 over those in the blanks were not sufficiently large to signify any change and are liable to error.

(4) Test with mixture - CO_2 - 95%, H_2 - 5%

Two litres passed in 15 minutes.

Flushing hydrogen contained no methane.

(5) Test with mixture - CO_2 - 80%, H_2 - 20%

and

(6) Two litres passed in 15 minutes.

Flushing hydrogen gas:-

	(5)	(6)
Volume -	0.8 litres	1.0 litres.
CH_4 % -	2.8	2.5

(7) Test with mixture - CO_2 - 85%, H_2 - 15%

Two litres passed in 15 minutes.

Flushing hydrogen gas - 1.0 litre, 2.5% CH_4

The above indicated that some methane was undoubtedly being formed/

formed, but being in such small amounts, estimation was liable to considerable error.

Since the above experiments showed some possibility of carbide formation, it was decided to continue the experiments after minimising the sources of error. A catalyst tube with a large capacity and with a minimum of free space on either side of the catalyst was employed. From one end a thermocouple sheath was introduced into the catalyst mass and heating was done in an electric tube furnace. (Figure 1).

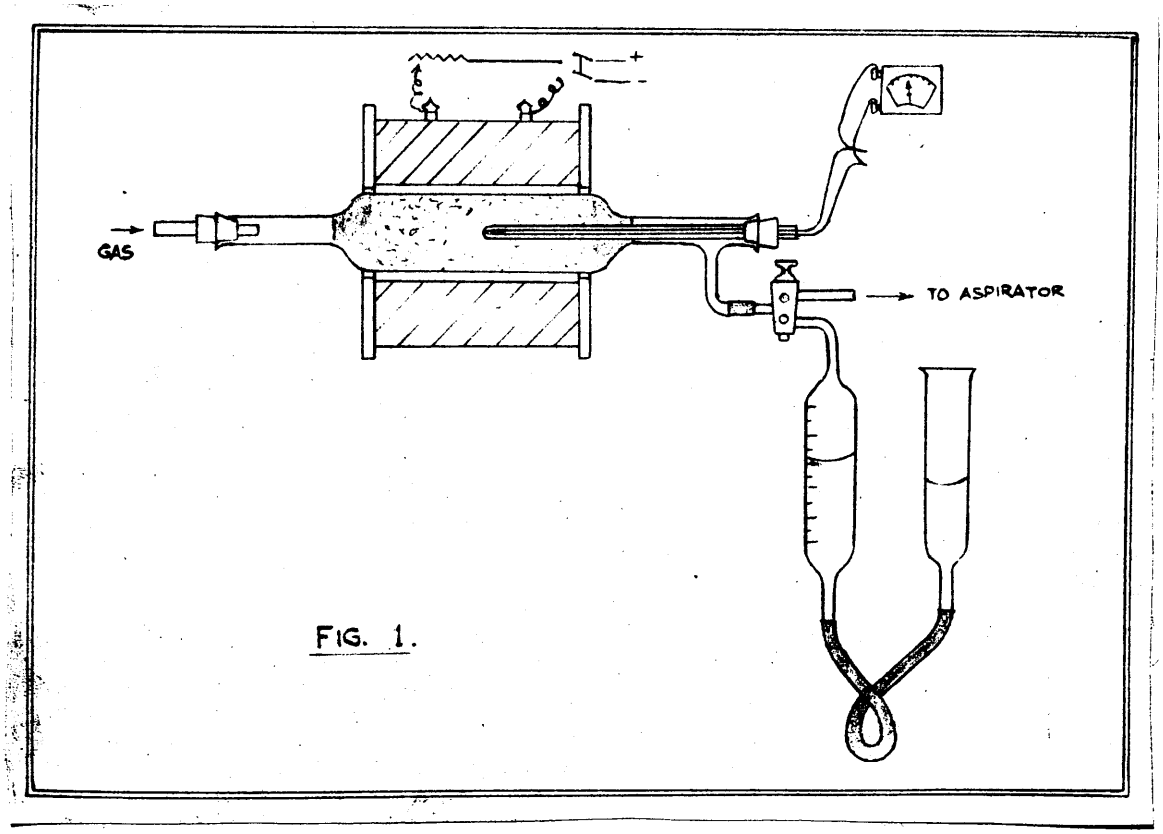

FIG. 1.

A long narrow gas-collecting tube with a two-way stop-cock was attached close to the outlet. The stop-cock enabled outgoing gas/

gas to be either collected in the sampling tube, or to be passed on to the aspirator as required. It was thus intended to minimise dilution with nitrogen and to collect only the first fraction of gas on passing hydrogen. It was expected that this would raise the methane content of the sample for analysis. In this series, the first two were blank runs.

(1) Blank run:- 40 ccs. Ni-ThO_2 I B cat. freshly reduced. Two litres CO_2 alone, passed for 15 minutes. Flushed with nitrogen. Hydrogen passed; product collected over fresh saturated brine.

Product gas:- 300 ccs.

	Macfarlane (analysis).	Bone & Wheeler (analysis).
CO_2	0.0%	0.0%
CH_4	0.0%	0.0%

(2) Blank run:-

Five litres CO_2 alone passed for 1 hour.

Product gas on passing hydrogen:- 300 ccs.

	Macfarlane	Bone & Wheeler.
CO_2	0.0%	0.0%
CH_4	0.0%	0.5%

(3) Above catalyst batch treated for 3 hours with 13.2 litres of CO_2 - 85%, H_2 - 15% mixture at a rate of 75 ccs./min. in two instalments. Analysis of product on/

production passage of first instalment of mixture

CO_2	-	92.0%
O_2	-	0.3
CO	-	0.3
CH_4	-	3.6
H_2	-	2.8
N_2	-	1.0
		100.0

Flushed with nitrogen and then hydrogen passed:-

Product gas:- 300 ccs.

	Macfarlane.	Bone & Wheeler.
CO_2	0.0%	0.0%
H_2	95.0	95.6
CH_4	1.4	1.7
N_2	3.6	2.7

(4) Catalyst treated for 70 minutes with 4.5 litres of CO_2 - 90%, H_2 - 10% mixture at 64 ccs./min.

Flushed with nitrogen and then hydrogen passed:-

Product gas:- 300 ccs.

	Bone & Wheeler.
CO_2	0.0%
H_2	97.5
CH_4	1.0
N_2	1.5

(5)/

(5) Catalyst treated with CO_2 - 85%, H_2 - 15% mixture for 4 hours.

16 litres passed in two instalments at 65 ccs./min.

Product gas on passing hydrogen:- 300 ccs.

Macfarlane.

CO_2 - 0.0%

H_2 - 96.0

CH_4 - 1.5

N_2 - 2.5

It is seen from the above experiments that even with improved technique, much longer treatment and much larger volume of catalyst, the concentration of methane formed in the final samples of gas could not be raised beyond the level where analysis errors could be neglected. The fact that methane was always detected in quantities greater than in the blanks, seems to suggest that treatment with CO_2 - H_2 mixtures had some effect. However, if that were the case, one would have expected that longer treatment and larger volume of catalyst would yield a higher concentration of methane on initial hydrogenation.

The formation of methane is definitely irregular and no definite conclusions can be drawn. Perhaps only an X-ray analysis could reveal such small quantities of carbide and distinguish it from elementary carbon.

It/

It must also be mentioned that when the catalyst batch used in the last five experiments was removed after use, it was found that about an inch of the front layers of catalyst had turned pale green. This was identified as carbonate and must have formed by the action of CO_2 on NiO. The front layers of catalyst due to insufficient heating must have remained in the unreduced state. A similar formation of carbonates on cobalt catalysts was suggested by Taylor and Burns (118), while studying the adsorption of carbon dioxide.

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CHAPTER II.

THE DECOMPOSITION AND HYDROGENATION OF METHANOL, FORMIC ACID AND FORMALDEHYDE.

Introductory.

Formic acid, formaldehyde and methanol have been suggested as possible intermediates in the synthesis of methane from carbon dioxide by several investigators. (39) (73)

It was therefore decided to study the decomposition and hydrogenation of these compounds over a nickel-thoria catalyst at synthesis temperatures, and to see whether such a study could elucidate their position as intermediates.

Eidus (119) found that methanol decomposes almost completely over a "Fischer-Tropsch" cobalt catalyst at 170-200°C., forming carbon monoxide and hydrogen. These react further to form small amounts of a mixture of liquid hydrocarbons. Formic acid similarly decomposes, chiefly to hydrogen and carbon dioxide, somewhat less to water and carbon monoxide, and very slightly to formaldehyde. Ethyl alcohol gives a series of products of which the chief are methane, carbon monoxide and hydrogen. In both cases liquid hydrocarbons are formed, but always as secondary products from carbon monoxide and hydrogen. Eidus concluded that these substances cannot therefore be intermediates in the synthesis of hydrocarbons from water gas. Unfortunately, the full publication was not available, and the above/

above is only an abstract. It is therefore not quite clear as to how this conclusion was arrived at.

In discussing the problem of the hydrogenation of the oxides of carbon, Armstrong and Hilditch (120) remarked - "We have confirmed Sabatier's observations (121) that formaldehyde is reduced to methanol in the presence of nickel (when it also suffers partial decomposition into carbon monoxide and hydrogen), but find that methanol is not converted to methane under similar conditions ..... so far as we have been able to ascertain, there is no evidence that hydrogenation of carbon dioxide or carbon monoxide goes in successive stages."

The decomposition of methanol has been extensively studied over oxide catalysts for methanol synthesis, over oxide catalysts for dehydrogenation to formaldehyde, and over metallic catalysts like iron, tin, aluminium, etc. Hydrogenation at high pressures and temperatures over nickel was studied by Ipatieff. (122) It was found under these conditions, that instead of obtaining methane and water, the latter oxidised methane to carbon dioxide. Armstrong and Hilditch (loc.cit.) reported that it was not possible to hydrogenate methanol to methane.

The decomposition of formic acid has also been the subject of considerable investigation. Sabatier and Maihle(123) studied the action of usual catalysts and found that formic acid/

acid decomposes in three ways:-

(1) $HCOOH = CO_2 + H_2$

(2) $HCOOH = CO + H_2O$

(3) $2HCOOH = HCHO + CO_2 + H_2O$

Nickel and copper induced reaction (1) almost exclusively, titania induced reaction (2) quantitatively, whereas with thoria both reactions (2) and (3) occurred. Hinshelwood and Tingey (124) studied the action of rhodium, gold and palladium which catalyse reaction (1), and Adkins and Nissen (125) investigated the selective dehydrating action of alumina. Wescott and Engelder (126) studied the decomposition of formic acid over unpromoted and unsupported nickel.

1 cc. of HCOOH yielded

°C	ccs. total gas.	ccs. CO_2	ccs. H_2	ccs. CO
210	327	157.6	152	18.6
257	490	235.0	220.5	34.6
353	873	453.0	395.5	36.7
455	814	365.0	311.0	138.0
524	801	283.0	257.0	262.0

No methane formation was observed by these investigators. Reinäcker and Bade (127) studied the action of copper-nickel alloys and found that pure nickel was more active than any alloy.

The/

The decomposition of formaldehyde vapour on various carbonates, oxides, metals, quartz and activated carbon was studied by Tropsch and Roehlen. (128) Over sodium carbonate and alumina, considerable amounts of methanol were produced. With uranium oxide some formic acid was obtained. Zinc oxide gave very few reaction products of high molecular weight; it decomposed dry formaldehyde to carbon monoxide and hydrogen and moist formaldehyde to carbon dioxide and hydrogen. In almost all cases, the formation of an oil with an odour of a terpene character was noticed. The hydrogenation of formaldehyde to methanol has been reported by Sabatier and Armstrong and Hilditch. (loc.cit.) Ipatieff and Monroe (66) studied the hydrogenation of formalin to methanol under high pressures over copper-alumina catalysts and concluded that the reaction proceeds in two ways:- (i) by direct hydrogenation, and (ii) by the Cannizzaro reaction - $2HCHO + H_2O = CH_3OH + HCOOH$.

It appeared, therefore, that on passing methanol, formic acid and formaldehyde vapours over a nickel-thoria catalyst at temperatures of about 290°C., these substances would decompose to a greater or less extent, giving mainly dehydrogenation products. Some of these products would then recombine to form methane. It was thought, however, that if the vapours were passed in a stream of hydrogen, the

decomposition/

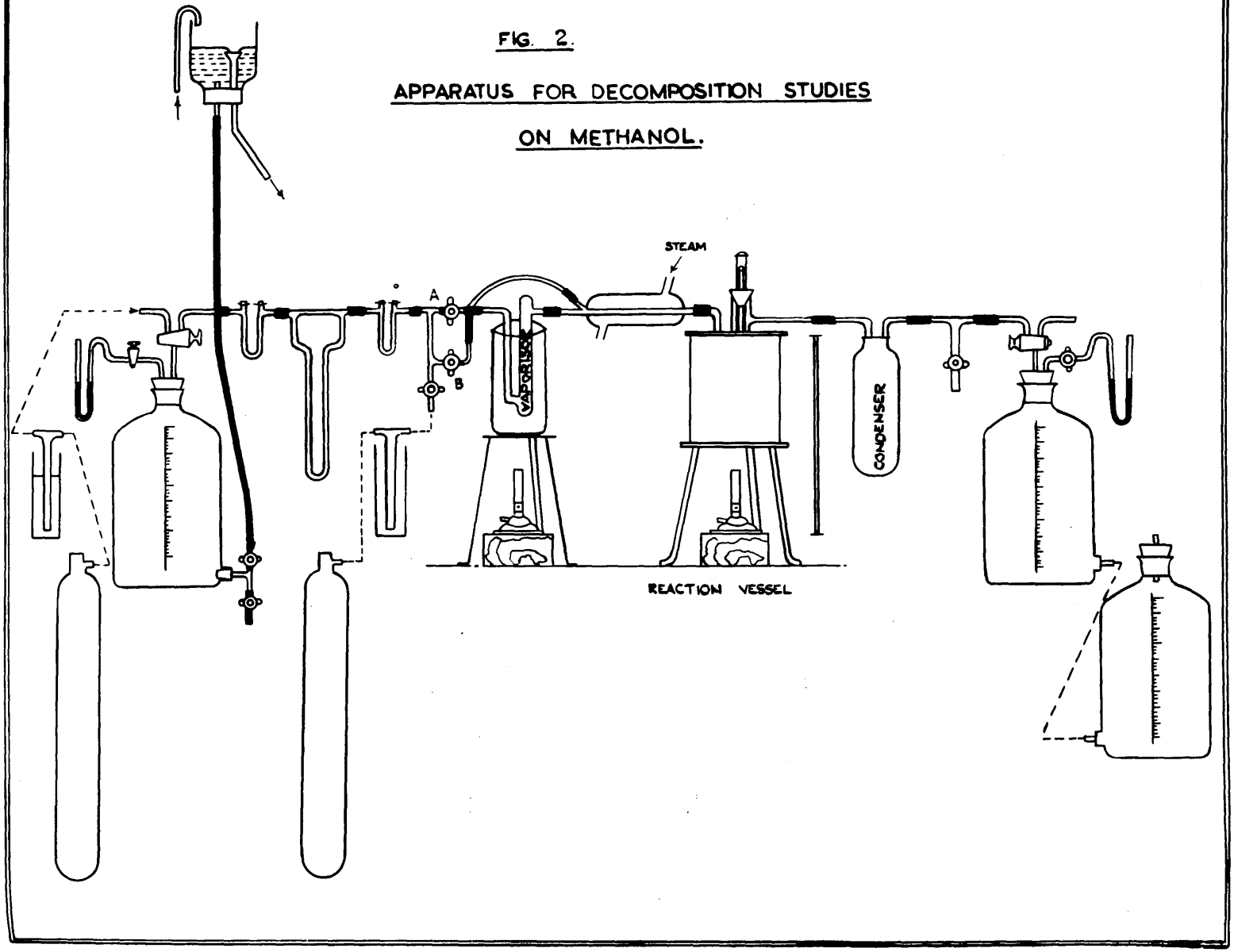
FIGURE 2.

APPARATUS FOR DECOMPOSITION STUDIES ON METHANOL.

FIG. 2.

APPARATUS FOR DECOMPOSITION STUDIES

ON METHANOL.



decomposition would be suppressed to a great extent and the substances would be hydrogenated to methane. If such hydrogenation occurred, there would be justification for considering methanol, formic acid and formaldehyde as intermediates in methane synthesis from carbon dioxide.

Other factors involved in this method of approach will be considered in the discussion of experimental results.

Experimental.

2. Description of Apparatus.

A sketch of the apparatus which was used for the studies described in this section is shown alongside. (Figure 2). The unit consisted of a constant-head device connected to a supply aspirator. The aspirator was provided with a two-way stop-cock for filling and delivery and fitted with a manometer. The delivery tube of the stopcock was connected to a flowmeter, through a drying $CaCl_2$ tube. The flowmeter was followed by a similar drying tube which was connected to a T-piece 'A'. One limb of the T-piece could be connected directly to the vapouriser, (described below) while the other was connected to a second T-piece, 'B'. One limb of T-piece 'B' could be connected directly to any gas cylinder, while the other limb joined on to the main system after the vapouriser. In this way, the vapouriser could be by-passed when required. The vapouriser - as shown in Figure 3 - consisted of a glass tube about/

about 6 inches long, provided with an outlet at the top and an inlet tube connected near the bottom.

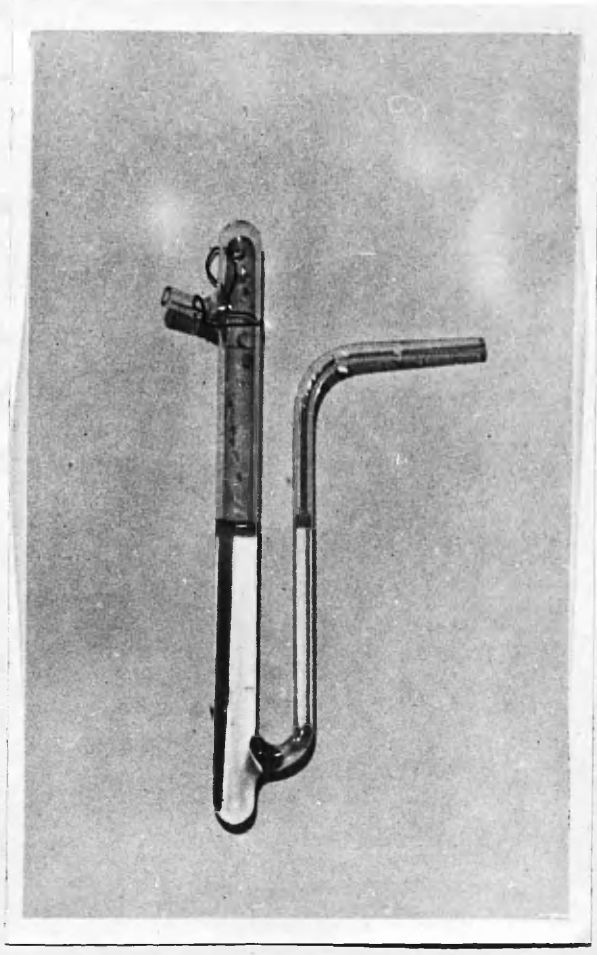


FIGURE 3.

The tube was immersed during runs in a water bath provided with a thermometer. Vapourisation was effected by bubbling nitrogen or hydrogen, or a mixture of the two, as required, through the liquid contained in the vapouriser. In order to prevent the vapours/

vapours from condensing before they reached the catalyst chamber, the connecting tube was steam-jacketted, steam being supplied from a small laboratory boiler. The catalyst chamber was identical with that described in Part I, and was immersed in an oil-bath.

The outlet of the catalyst chamber was connected to a spiral condenser with a collecting bulb at the bottom. The condenser was cooled with solid carbon dioxide in a thermos flask. The condenser served to trap undecomposed vapours and other condensible products that were formed. The non-condensible gases then passed on to the collecting aspirator, which was provided with a two-way stop-cock and a manometer. The gases were collected over saturated brine containing 1 per cent. sulphuric acid. A side-tube with a stop-cock was included between the condenser and the collecting aspirator, to enable the system to be flushed out when required. Both the aspirators were carefully graduated.

3. Experiments with Methanol.

The methanol as obtained was first tested for the presence of acetone. Both Legal's nitroprusside test and the Salicylaldehyde test failed to reveal the presence of acetone. Since it was already of a high degree of purity, the simplest way of obtaining absolute methanol was followed. By adding a small/

small quantity of pure magnesium to a portion of the alcohol, a suspension of magnesium methylate was obtained. To this the rest of the alcohol was added and refluxed for four hours. In this way, any trace of water present reacted to give insoluble magnesium oxide.

$$(MeO)_2\ Mg + H_2O \longrightarrow 2\ MeOH + MgO$$

The alcohol was then distilled off and stored.

Procedure:- The vapouriser was filled with methanol up to a mark, the two outlets were stoppered with rubber tubing and pieces of glass rod, and the filled tube was weighed. The nickel-thoria catalyst was reduced with hydrogen in the usual way. Before a run, the catalyst was heated up to the required temperature in a stream of hydrogen. In the case of decomposition experiments, the hydrogen in the system was replaced by a stream of nitrogen before connecting the vapouriser on to the system. The inlet tube of the vapouriser was then connected to the system; a few ccs. of the gas (N_2 or H_2) was bubbled through it in order to replace the air as far as possible without undue loss of methanol. The outlet tube was then quickly connected on to the steam-jacketted inter-connecting tube and the vapouriser immersed in the water bath. The run was then started by allowing the vapourising gas to bubble through the alcohol at the desired rate. Each run was timed/

timed with a stop-watch and the volumes of gas passed and collected were noted. After a run, the methanol vapouriser and condenser were immediately disconnected, stoppered, cooled and weighed. The product gas was sampled and analysed. The weight of the product gas was calculated from its composition and the total volume produced, and added to the weight of the condensate. This was balanced against the weight of methanol vapourised. In the case of decomposition runs, the nitrogen was not taken into account, while for hydrogenation runs, the weight of hydrogen supplied had to be accounted for.

Errors in mass balance could have arisen from (i) errors in noting volumes of gas passed and collected, (ii) errors in analysis, and (iii) loss of methanol while connecting and disconnecting the vapouriser. In certain cases, these errors might have cancelled each other.

During gas analysis in the present and following series of experiments, it was sometimes found that, due to high dilution with nitrogen, the residual gas failed to explode. In such cases it was found necessary to first estimate the carbon dioxide, oxygen and carbon monoxide contents. A fresh sample of gas was then taken, the carbon dioxide and oxygen removed and the carbon monoxide retained for the explosion mixture. The following equations were then applied:-

H_2/

TABLE I.

TABLE I.

Decomposition and Hydrogenation of Methanol.

Catalyst - Ni - ThO_2 IB. (8.2 ccs.)

Expt. No.	Gas Passed.	Rate of flow ccs/min.	MeOH vapd./ min. gms.	Cat. Temp. °C.	Product Gas Compsn. % CO_2	O_2	CO	CH_4	H_2	N_2	Prod. Volume Collctd. litres.	Room temp. °C.	Bar. press. mm. Hg.	Time of Run mins.	Mass Balance %
1	N_2	75	.0465	285	0.1	0.9	13.5	8.3	17.1	60.1	3.65	20	757	27.0	Trial runs.
2	N_2	80	.0503	280	0.1	0.8	11.6	11.8	8.8	66.9	3.50	19	760	25.0	
3	N_2	85	.0646	285	0.4	0.2	12.7	11.5	11.7	63.5	3.60	19	759	23.0	
4	N_2	75	.0267	285	0.4	0.3	11.5	2.4	22.1	63.3	4.89	15	750	40.5	- 2.5
5	N_2	70	.0258	285	0.3	0.3	12.2	3.2	23.1	60.9	7.26	15	745	62.5	- 2.5
6	N_2	75	.0454	285	0.1	0.4	14.0	4.2	25.4	55.9	4.77	16	760	34.5	- 3.0
7	N_2	80	.0618	285	0.4	0.3	15.3	12.2	21.2	50.6	4.24	14	757	25.0	- 2.0
8	H_2	86	.0656	288	0.4	0.4	13.7	7.2	77.1	1.2	4.26	16	750	29.0	- 0.8
9	H_2	81	.0637	285	0.5	0.2	14.5	4.2	79.0	1.6	3.64	18	750	25.0	- 1.5
10	H_2	77	.0664	285	0.5	0.4	13.3	5.5	79.0	1.3	6.75	16	760	52.2	- 0.2
11	H_2	154	0.148	285	0.4	0.6	11.9	10.2	76.0	1.0	3.00	14	757	13.0	- 5.0

TABLE I A.

TABLE IA.

Decomposition and Hydrogenation of Methanol.

Expt. No.	MeOH conctrn. -4 gms. x 10 per cc. of gas.	MeOH vaprsd. gms.	Equivlt. wt. of CO.gms.	Equivlt. wt. of CO. in product. gms.	% Decomposed to gas.	% of Decompsn. Converted to CO + CO_2	% of Decompsn. Converted to CH_4	Ratio H_2/CO in system.	Remarks.
1	6.28	1.255	1.098	0.934	85.2	62.0	38.0	2	Trial Runs
2	6.29	1.260	1.110	0.932	84.0	49.8	50.2	2	
3	7.42	1.472	1.288	1.030	80.0	53.2	46.8	2	
4	3.16	1.084	0.948	0.820	86.5	83.5	16.5	2	Decomposition Runs
5	3.75	1.614	1.411	1.330	94.4	79.7	20.3	2	
6	6.10	1.567	1.368	1.028	75.2	76.8	23.2	2	
7	7.72	1.547	1.350	1.380	100.0	56.4	43.6	2	Fresh cat.
8	7.61	1.901	1.662	1.058	63.5	66.3	33.7	4.8	Hydrogenation Runs
9	7.88	1.697	1.482	0.807	54.5	78.25	21.75	4.9	
10	8.75	3.129	2.736	1.540	56.3	71.5	28.5	5.1	
11	9.60	1.931	1.692	0.794	47.0	54.8	45.2	5.0	Fast rate of flow

$H_2 = C - x$

$CO = 2/3\ (2A + \frac{1}{2} H_2 - x)$

$CH_4 = A - CO$

where C = contraction after explosion, A = CO_2 formed, x = oxygen used.

Results:

The condensate in the methanol runs showed no side products and only a trace of formaldehyde was observed in one case. The main decomposition therefore was to gaseous products, as shown by the analyses figures in Table I. These products contained no unsaturated or higher saturated hydrocarbons, as is to be expected under the conditions employed. The decomposition was presumably one of straight dehydrogenation to carbon monoxide and hydrogen, followed by appreciable formation of methane; only traces of carbon dioxide were produced.

A summary of the results is shown in Table IA. The percent decomposition has been calculated on the basis of equivalent weight of carbon monoxide in the methanol passed, and the weight of total carbon containing gas in the product, expressed in terms of carbon monoxide. A general comparison of the decomposition runs 1-7 and hydrogenation runs 8-11, shows that the decomposition was to some extent suppressed in an atmosphere of hydrogen. Theoretically, introduction of hydrogen has an effect on the equilibrium. In the equation for methanol decomposition:/

decomposition:-

$$\underset{a}{CH_3OH} \qquad \underset{b}{2H_2} + \underset{c}{CO}$$

$$K_c = \frac{b^2 c}{a} \text{ (constant volume)}$$

If the reaction is carried out in the presence of excess hydrogen, suppose x, then the new volume of hydrogen now becomes (b + x). Let a' and c' be the new concentrations of CH_3OH and CO,

$$\text{then} \quad K_c = \frac{(b + x)^2 \, c'}{a'}$$

$$= \frac{(b^2 + 2bx + x^2)}{a'} \, c'$$

for K_c to be constant, b must be reduced to b', and therefore the reaction will be retarded. However, at 300°C., equilibrium is overwhelmingly in favour of H_2 and CO, (K_c being about 6.3 x 10^3) and excess of hydrogen will not have a marked effect. Moreover, any effect on the equilibrium would probably be more readily noted in a homogeneous system. In a heterogeneous reaction, concentrations on the catalyst surface may be quite different from those in the gas phase and will depend on the respective adsorptions. It may happen that out of two components, one is very much more strongly adsorbed than the other. In that case, varying gas compositions over a small range will hardly have any effect and the strongly adsorbed component will continue to occupy the major portion of the surface. In other cases, increase of one component will tend

to/

to displace the other.

It appears therefore that the total decomposition of methanol is suppressed to some extent in an atmosphere of hydrogen, because less of the catalyst surface is now available for the methanol molecules to react upon. It will also be noticed that the amount converted to methane on introducing hydrogen was not appreciably raised. This indicates that under these conditions, whatever hydrogenation takes place is really by the interaction of carbon monoxide and hydrogen, rather than by direct hydrogenation of methanol.

4. Experiments with Formic Acid.

The procedure was in general the same as that employed for the methanol experiments. The formic acid used was of 98 per cent. strength.

Formic acid starts decomposing beyond about 170°C. and can decompose like an acid into CO_2, or like an aldehyde into CO: (129)

$$H - COOH \longrightarrow H_2 + CO_2$$

or

$$H - O - CHO \longrightarrow H_2O + CO$$

Müller (129) assumed that the decomposition into hydrogen and carbon dioxide proceeds through a metastable form. This is represented as:-

H/

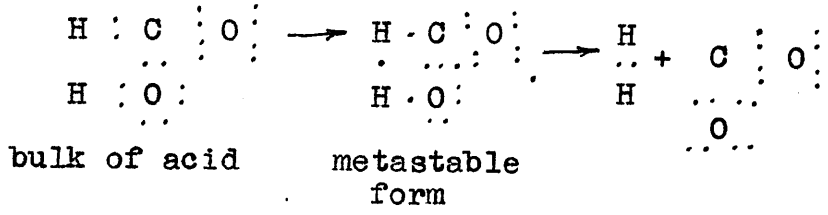
TABLE II.

TABLE II.

Decomposition and Hydrogenation of Formic Acid.

Catalyst - Ni - ThO_2 IB (8.2 ccs.)

Expt. No.	Gas Passed.	Time of Run mins.	Rate of Flow ccs/min.	HCOOH vapd./ min. gms.	Cat. Temp. °C.	Product Gas Compsn. % CO_2	O_2	CO	CH_4	H_2	N_2	Product Volume Collctd. Litres.	Room temp. °C.	Bar. press. mm. Hg.	Mass Balance %
1	H_2 Thermal decompsn.	40	62.5	0.055	290	1.24	0.2	0.0	0.0	98.2	0.36	2.62	15.0	744	-5
2	N_2	36	76.0	0.117	290	25.8	0.4	1.0	11.3	10.5	52.3	5.42	14.0	750	-2 -Trial
3	N_2	36	74.0	0.0844	288	24.8	0.1	2.1	3.7	18.1	51.0	5.10	12.5	730.5	-2.5
4	50% H_2 + 50% N_2	38	60.0	0.0623	290	24.7	0.2	0.3	7.1	37.7	30.0	3.75	14.5	747.5	-1.3
5	H_2	35	80.0	0.0417	290	15.8	0.8	0.3	4.8	76.7	1.6	3.55	14.0	737.5	-1.9
6	H_2	36	66.0	0.068	290	24.7	0.5	0.8	15.6	57.2	1.2	3.00	14.0	750	-4.0 Trial
7	H_2	36.5	62.0	0.0758	290	27.6	0.3	0.6	10.82	59.4	1.3	3.67	13.0	738	±0.0
8	H_2	40.0	62.5	0.0847	290	28.1	0.4	0.6	10.82	58.3	1.8	4.10	14.0	753	-7.0
9	H_2	99.3	20.0	0.033	290	30.2	0.5	2.0	6.3	59.1	1.9	4.25	16.0	737	-5.0



bulk of acid metastable form

Engler and Grimm (129) stated that at 169°C. formic acid is completely transformed into water and carbon monoxide, and Noyes and Wobbe (130) reported that at 170°C. the acid decomposes very slowly.

Because of this tendency for thermal decomposition, it was necessary to test how far the decomposition would proceed under the experimental conditions employed. In Experiment 1, Table II, the formic acid was vapourised in a stream of hydrogen and passed through the reaction chamber packed with asbestos wool instead of catalyst. Under these conditions, only a 3 per cent. decomposition into CO_2 was noted. A second run in which the volumes of gas passed and collected were noted, also showed no great change. It is difficult to explain why this thermal decomposition was suppressed. The contact time is an important factor. The hydrogen atmosphere and the presence of 2 per cent. water in the acid may have exercised a retarding influence. It is also possible that the acid vapours did not attain a high temperature, but this is very unlikely. It can however be inferred that in all the subsequent experiments the decomposition was mainly catalytic.

It/

TABLE II A.

TABLE IIA.

Decomposition and Hydrogenation of Formic Acid.

Expt. No.	HCOOH concntrn. gms. x 10^{-4} per cc. of gas.	HCOOH vaprsd. gms.	Corrctd. Equvlt. wt. of CO_2 gms.	Equvlt. wt. of CO_2 in product gms.	% Decomp-osed to gas.	% of Decompsn. Converted to CO_2+ CO.	% of Decompsn. Converted to CH_4.	Ratio H_2/CO_2 in system.	Remarks.
1	8.74	2.1866	2.04	0.06	3.0	100.0	0.0		Thermal Decomposition.
2	14.87	4.09	3.83	3.80	100.0	69.8	30.2	1	Catalytic Decomposition.
3	11.52	2.999	2.72	2.63	96.5	87.0	13.0	1	
4	11.00	2.3652	2.22	2.20	99.2	77.6	22.4	1.94	Gas stream 50 H_2 : 50 N_2
5	5.25	1.442	1.35	1.33	98.4	76.8	23.2	4.77	Hydrogenation
6	10.40	2.443	2.29	2.24	98.0	61.2	38.8	2.95	
7	12.27	2.764	2.59	2.585	99.6	71.8	28.2	2.59	
8	13.55	3.3878	2.97	2.97	100.0	72.2	27.8	2.56	
9	16.38	3.2684	2.98	2.97	99.6	83.7	16.3	2.24	Slow rate of flow.

It is seen from Table II A that the percentage decomposition was high in all cases, ranging from 96-100 per cent. The decomposition was mainly one of dehydrogenation with a small amount of dehydration to carbon monoxide, as is shown in the analysis figures in Table II. Even in a nitrogen stream, there was an appreciable formation of methane, which must have formed by the interaction of the products, carbon dioxide and hydrogen. On introducing 50 per cent. of hydrogen along with the nitrogen, (Experiment 4) the methane formation was increased to a marked extent - but the subsequent experiments show that further increase of hydrogen in the system did not result in any large increase in hydrogenation, nor was the total amount of decomposition reduced in any way. It would appear, therefore, that hydrogen does not displace the acid molecules from the catalyst surface, and that whatever methane formation takes place is largely due to interaction between carbon dioxide and hydrogen formed by decomposition, rather than by direct hydrogenation of formic acid.

5. Experiments with Formaldehyde.

The experimental procedure was in general the same as that described for the experiments with methanol and formic acid.

Pure, dry formaldehyde cannot be obtained by the fractional/

fractional distillation of formalin solution. Paraformaldehyde has been used as a source of formaldehyde (128) for such experiments, and under the circumstances, it seemed the simplest way of obtaining formaldehyde vapour. There is, however, one great drawback - namely, that paraformaldehyde contains water which cannot be driven off by ordinary methods. As far as possible, the water was removed by first heating the paraformaldehyde in a basin in an air oven at 120°C. for about an hour. This resulted naturally in considerable loss, but was unavoidable. It was then dried over fresh P_2O_5 in a vacuum desiccator for three days. The paraformaldehyde, which was in powder form, was then pelletted and again stored over P_2O_5 for two days before use. Vapourisation of these pellets was effected by heating in a current of nitrogen or hydrogen as required. For the first few runs, (Experiments 1 - 6, Table III) vapourisation was carried out in a tube similar to the methanol vapouriser, (Figure 3 , page 182) except that the tube was open at the top to enable the pellets to be introduced. This opening was then stoppered with a bung. The pellets rested on asbestos wool, and were covered by a layer of the same in order to prevent solid particles of paraformaldehyde from escaping into the gas stream. The vapouriser was connected to the catalyst chamber by the interconnecting steam-jacketted tube, and was heated by an air bath.

The/

TABLE III.

TABLE III.

Decomposition and Hydrogenation of Formaldehyde.

$Ni-ThO_2$ Catalyst IB.

Expt. No.	Gas Passed.	Rate of flow. ccs/min.	Cat. temp. °C.	Product Gas Compsn. % CO_2	O_2	CO	CH_4	H_2	N_2	Product Volume Collctd. litres.	Ratio H_2/CO in system.	% converted to CO_2	CO	CH_4	Remarks.
1	N_2	100	290	1.3	0.4	11.4	3.1	10.4	73.4	2.10	1.0	8.4	72.2	19.4	(8.2 ccs. cat.)
2	H_2	110	290	2.1	0.5	0.5	18.6	77.0	1.7	1.78	5.7	9.6	2.4	88.0	
3	H_2	110	290	1.2	0.7	0.0	13.2	83.5	1.4	2.38	8.3	8.4	0.0	91.6	
4	H_2	100	290	0.3	0.6	0.0	5.7	90.6	2.8	2.00	17.6	5.3	0.0	94.7	Trial runs Very low concns.of HCHO.
5	H_2	110	285-90	0.2	0.7	0.0	6.0	91.2	1.9	1.81	18.0	3.9	0.0	96.1	
6	H_2	100	290	0.0	0.5	0.0	5.8	92.7	1.0	1.87	18.4	0.0	0.0	100.0	
7	N_2	227	285	1.5	0.4	15.3	3.4	14.7	64.7	4.05	1.0	7.6	75.5	16.9	(10 ccs. at.)
8	H_2	230	285	1.6	0.5	18.8	5.1	73.0	1.5	4.25	2.8	6.2	73.8	20.0	
9	N_2	170	290	1.3	0.4	18.5	3.2	14.2	62.5	3.60	1.0	5.5	80.5	14.0	
10	H_2	175	290	1.0	0.4	19.1	4.1	73.7	1.7	3.50	3.6	4.1	79.0	16.9	
11	H_2	170	290	0.2	0.4	11.5	6.7	79.2	2.0	4.78	4.7	1.2	62.3	36.5	
12	CO_2- 33% H_2 - 66%	170	290	23.8	0.4	11.5	6.0	57.0	1.2	2.83	3.88	2.0 assumed	68.0	31.0	4% CO_2 in gas convtd.
13	CO_2- 34% H_2 - 66%	170	290	28.5	0.5	4.4	6.4	58.5	1.7	2.66	6.40	1.0 assumed	40.8	58.2	1% CO_2 in gas convtd.
14	CO_2- 34.5% H_2 - 65.0%	170	290	35.0	0.4	0.0	5.3	58.5	0.8	2.60	-	-	-	14.5	- no HCHO in system. 14.5% CO_2 in gas cvtd.

The same coiled condenser immersed in solid carbon dioxide was used in order to trap any liquid products. It was obvious that undecomposed gaseous formaldehyde might still pass over to the gas collecting aspirator. A water scrubber would therefore have been desirable, but it would also have trapped any CO_2 that might be formed. In order to find whether under the conditions employed, any undecomposed formaldehyde got past the condenser, some tests were done by attaching a water bubbler after the condenser and letting the gases flow out to the atmosphere. Out of three such tests, only a trace of formaldehyde was detected in one case.

The decomposition of formaldehyde, both in nitrogen and hydrogen streams, led to gaseous products and only a trace of methanol could be detected in the condensate in the case of Experiment No. 10. The gaseous products consisted of CO_2, CO, CH_4 and H_2, and no unsaturated or higher hydrocarbons were found. The mass balance errors were very high. (-7 to -10 per cent). This was due to some paraformaldehyde recondensing on the interconnecting tubes.

For purposes of comparison, it has been considered sufficient to express the experiments of this series, only in terms of the H_2/CO ratio in the system. For decomposition runs this ratio of available hydrogen to available carbon monoxide will/

will be unity (i.e., the ratio in which they are present in the HCHO molecule). For the hydrogenation runs, the ratio has been obtained by first finding the total CO in the system from the total carbon-containing gas in the product; the total hydrogen in the system will be the amount of hydrogen passed, plus an amount equal to the quantity of CO, being derived from the breaking up of the HCHO molecule.

Experiments 1 - 6 (Table III) show that on passing the formaldehyde in a stream of nitrogen, (Experiment 1) an appreciable amount of methane was formed, by interaction of CO and H_2, produced by the breaking up of the formaldehyde molecule. Some CO_2 was also formed, possibly by the reaction:-

$$2\,CO + 2H_2 = CO_2 + CH_4 \quad (i)$$

What is surprising is that even in the presence of a large amount of hydrogen, the formation of CO_2 persisted. That would suggest that CO_2 formation occurred, not by reaction (i) alone, but also by the water gas shift reaction :-

$$CO + H_2O = CO_2 + H_2 \quad (ii)$$

In experiments 3 - 5, although there was complete disappearance of CO in the product gas, the presence of CO_2 indicates that some free CO must have been formed. The only other possible source of CO_2 is the methane steam reaction

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$$

but this is unlikely, because at these temperatures, the equilibrium/

equilibrium is very much in favour of methane and water. In other words, it appears that even in the presence of a large amount of hydrogen, some of the formaldehyde must have been decomposing into CO and H_2. It is, however, not possible to judge whether the major portion of methane formation was occurring by the direct hydrogenation of formaldehyde, or by the interaction of products, following decomposition.

Experiments 7 - 14 were conducted at a later date. In these experiments the method of vapourisation of paraformaldehyde was altered. The oil-bath was replaced by an electric tube furnace and the catalyst was placed in a pyrex glass tube of 3/4 inch diameter. (Figure 4).

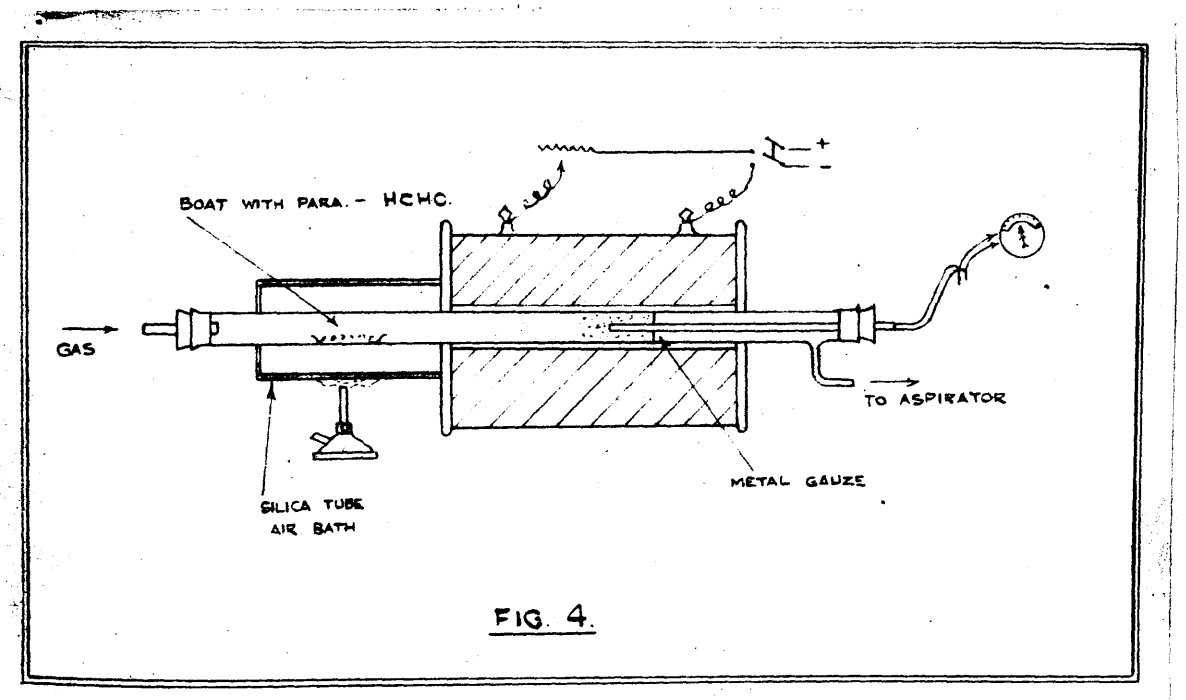


FIG. 4.

FIGURE 4.

The catalyst was supported at one end by a monel metal gauze disc through which passed the thermocouple pocket. On the other side the catalyst was supported by some ignited asbestos wool. The pelletted paraformaldehyde was placed in a porcelain boat. The vapouriser was an air bath heated by a bunsen burner. It consisted of a silica tube covered at the ends with asbestos paper, and was provided with a thermometer. Ten ccs. of Ni-ThO_2 catalyst I B were used in these experiments.

Experiments 7 and 9 were decomposition runs, whereas Experiments 8, 10 - 13 were hydrogenation runs. It will be noticed that there was appreciable increase in methane formation on introducing hydrogen, but large amounts were decomposed straight to CO and some CO_2 was always formed. The CO_2 formation was reduced on increasing the H_2/CO ratio in the system. Experiments 12 - 14 were conducted in order to find how far the surface of the catalyst was covered with formaldehyde. Instead of using pure hydrogen in the vapourising stream, a mixture of 33 per cent. CO_2 and 66 per cent. H_2 was used. Assuming that about 1 - 2 per cent of the formaldehyde was converted to CO_2, the rest of the CO_2 in the product gas was balanced against the amount that was passed, and it was found that only 1 - 4 per cent. of the CO_2 was converted to methane. The amount of conversion was probably even less, because/

because generally there is a slight loss in CO_2 recovery in such experiments. Experiment 14 was made without any formaldehyde in the system and the conversion of CO_2 to methane was 14.5 per cent., very much higher than in Experiments 12 and 13. This indicated that under the conditions employed, practically all the surface of the catalyst was covered with formaldehyde, or by CO produced by breaking up of HCHO. A study of the percentage conversion of formaldehyde to methane indicates that the presence of carbon dioxide had no retarding influence on the decomposition and hydrogenation of formaldehyde, and the catalyst surface being otherwise covered, there was no space left on which the adsorption and hydrogenation of carbon dioxide could proceed.

These general studies indicate that methanol, formic acid and formaldehyde are preferentially decomposed rather than hydrogenated over a nickel-thoria catalyst at temperatures of about 290°C. Hydrogenation occurs rather by the interaction of decomposition products.

There are several limitations in this method of approach and it does not necessarily mean that these substances cannot occur as intermediates in methane synthesis from carbon dioxide. Whenever such intermediates occur, they are produced transitorily and their orientation on the catalyst surface may be such that the sequence of steps culminating in the final product/

product is easily accomplished. On the other hand, when the same substances are made to condense on the catalyst surface from the gas phase, they may be oriented in a way which favours dehydrogenation. Furthermore, if these substances tend to cover the catalyst surface and do not allow sufficient hydrogen to be present, the tendency will again be towards dehydrogenation. All these factors will be more fully considered in the final discussion.

Lastly, there is the question of the activity of the catalyst. A catalyst which is not very active in hydrogenation may be active in dehyrodgenation, and may therefore preferentially decompose rather than hydrogenate. A catalyst with higher hydrogenating capacity will carry the hydrogenation to a further extent, as was found with some experiments on a "Fischer-Tropsch" catalyst described hereafter. Wescott and Engelder (126) (loc.cit.) obtained no methane in their studies on the decomposition of formic acid, because they used an unsupported and unpromoted nickel catalyst which must therefore have been relatively weak in its hydrogenating capacity even at high temperatures.

6. Experiments with a "Fischer-Tropsch" Catalyst.

(a) The interaction of carbon dioxide and hydrogen.

A cobalt-thoria-magnesia-kieselgurh catalyst active in the synthesis of higher hydrocarbons, was obtained by courtesy of/

of the Fuel Research Station, Greenwich. It had the following composition:-

Co	ThO_2	MgO	Kieselgurh	(parts by weight).
100	6	12	200	(as prepared)
100	6	3	200	(as found by analysis).

It was reduced at 400°C. for two hours with a hydrogen rate of 2 cu.ft./hour for 10 ccs. of catalyst (as instructed).

The catalyst was tested for its activity towards the hydrogenation of carbon dioxide, as shown in the following Table IV. It was found difficult to control the temperature. In some of the experiments the temperatures were higher than was intended. This was due to a defect in the millivoltmeter used for recording the temperatures. The corrected values after subsequent calibration have, however, been recorded.

The catalyst was thus quite active at various temperatures. Experiments 1 and 2 show that it was much more active than the nickel-thoria catalyst batch used for the formaldehyde studies. (Table III, 7 - 14). The nickel-thoria catalyst under similar conditions gave a 14.5 per cent. conversion, whereas the "Fischer-Tropsch" catalyst gave a 38 per cent. conversion.

TABLE IV/

TABLE IV.

Cat. Volume - 10 ccs.
Cat. weight - 5.7 gms. (unreduced)
Yield expressed as:- Ccs. CH_4 formed/cc. cat./min.

Expt. No.	Gas Compsn. per cent. CO_2	H_2	Rate of Flow. ccs./min.	Temp. °C. (average)	Per cent. Conversion.	Yield.	Balance CO_2 recovery per cent.
1	33.0	66.0	175	290	38.0	2.2	97.0
2	34.0	65.0	175	295	37.0	2.14	98.0
3	40.8	58.1	290	290	25.8	3.07	96.6
4	40.0	59.0	250	230	10.7	1.11	97.5
5	28.0	71.0	200	240	24.5	1.08	98.0
6	28.0	71.0	150	200	11.6	0.35	97.0
7	25.0	74.5	300	298	58.0	4.06	97.5
8	25.0	74.5	300	250	30.0	2.12	98.0

Experiments 4, 5 and 6 (Table IV) show that there was good conversion even at as low temperatures as 200-240°C. The catalyst was further tested with CO_2 - H_2 mixtures in order to find whether any hydrocarbons higher than methane could be formed by keeping the temperature low and allowing sufficient time. Two such/

such runs were carried out in the pressure plant, described in Part II. The first run was at atmospheric pressure and the other at 10 atmospheres.

Experiment (i)

Synthesis Gas:- CO_2 - 30% Cat. volume:- 30 ccs. } unreduced
H_2 - 70% Cat. weight:- 18.0 gms }

Pressure:- Atmospheric.

Temperature:- 200°C. (approx). (Reduced at 400°C.)

Run continuously for 46 hours.

Overall average rate of flow:- 1.85 litres/hour.

Outlet samples taken at intervals and analysed:-

	After 6 hrs. %	After 20.5 hrs. %	After 30 hrs. %	After 44 hrs. %
CO_2 -	33.15	34.2	33.7	36.6
O_2 -	0.41	0.41	0.2	0.72
CO -	0.41	0.20	0.0	0.31
CH_4 -	2.83	4.30	2.66	9.84
H_2 -	62.40	60.20	62.50	51.55
	99.20	99.31	99.10	99.02

No unsaturateds or higher hydrocarbons were found. These analyses are somewhat misleading, because although each sample was taken over a period of about 45 minutes, the rates of flow at these periods were not quite the same. The variations in methane content might be accounted for in that way.

Experiment (ii)/

Experiment (ii)

Synthesis Gas:- CO_2 - 33% Same catalyst batch as in
H_2 - 66% Experiment (i)

Pressure:- 10 atmospheres.

Temperature:- 200-220°C.

Run continuously for 25 hours.

Overall average rate of flow:- 3.8 litres/hour. (At atmos. press).

Instead of sampling gas at intervals, a sample was taken after 25 hours.

Analysis:-		%
	CO_2 -	38.3
	O_2 -	0.4
	CO -	0.5
	CH_4 -	13.6
	H_2 -	46.1
		98.9

No unsaturateds or higher hydrocarbons were found.

When the silica gel in the water trap was removed after use and heated in a distilling flask, the water that was collected had a smell like that of dilute methyl formate. The amount was too small to be identified.

(b) The decomposition and hydrogenation of formaldehyde.

The procedure was the same as that described for the experiments with the nickel-thoria catalyst. The results are summarised in Table V. Temperature control was found to be difficult/

TABLE V.

TABLE V.

Decomposition and Hydrogenation of Formaldehyde.

Co - ThO_2 - MgO - Kieselgurt
"Fischer - Tropsch" synthesis catalyst.
Cat. volume - 10 ccs.
Cat. weight - 5.7 gms. (unreduced).

Expt. No.	Gas passed.	Rate of Flow. ccs/min.	(Average) Cat. temp. °C.	Product Gas Compsn. % CO_2	O_2	CO	CH_4	H_2	N_2	Product volume collctd. litres.	Equivlt. CO concn. in gas. ccs/cc. gas passed.	Ratio H_2/CO in system.	% converted to CO_2	CO	CH_4	Remarks.
1	N_2	140	290 (a)	6.0	0.4	2.6	6.8	2.6	81.6	2.875	0.2	1	39.0	17.0	44.0	
			(b)	6.0	0.4	2.6	7.4	2.7	80.9							
2	N_2	140	200 (a)	3.1	0.1	10.3	4.6	6.7	75.2	2.87	0.23	1	17.2	57.0	25.8	
			(b)	3.4	0.1	10.0	4.3	7.0	75.2							
3	N_2	140	220	0.3	0.8	19.3	8.9	13.1	57.6	3.91	0.56	1	5.1	67.7	31.2	
4	H_2	150	220	9.5	0.75	7.7	38.4	43.0	1.4	2.50	0.55	2.6	17.1	13.8	69.1	
5	H_2	150	220	4.1	0.3	13.1	25.7	55.7	1.1	3.58	0.56	2.9	9.5	30.4	60.1	
6	H_2	150	230	10.2	0.4	2.6	40.8	45.0	1.0	2.37	0.50	2.9	19.0	4.9	76.1	
7	H_2	150	290	11.4	0.8	1.06	45.7	40.2	0.84	2.25	0.52	2.9	19.5	1.9	78.6	fresh cat.
8	H_2	110	300	15.7	0.5	0.2	44.2	38.8	0.8	2.42	0.65	2.6	26.0	0.4	73.6	slower rate of flow.

difficult and there was always a rapid initial rise. The average corrected values have been recorded. The condensate in all these experiments was water with a faint aromatic odour. The main decomposition was to gaseous products. These contained no unsaturated hydrocarbons. The hydrogenation runs showed no hydrocarbons higher than methane. This is not surprising in view of the fact that there were temperature fluctuations, and that the runs were of short duration. (About 20 minutes). During Fischer-Tropsch synthesis, it is known that several hours are required before the catalyst becomes "normalised" and the synthesis of higher hydrocarbons begins.

Large quantities of CO_2 formation were noted in almost all cases, except in Experiment 3 which is peculiar in this respect. The CO_2 could have formed by the reaction:-

$$2\,CO + 2H_2 = CO_2 + CH_4 \quad (i)$$

or by the water gas shift reaction:-

$$CO + H_2O = CO_2 + H_2 \quad (ii)$$

If it is assumed that reaction (i) is operating and that the rest of the methane is formed by the reaction:-

$$CO + 3H_2 = CH_4 + H_2O \quad (iii)$$

then the product gas compositions in experiments 1 and 2 can be analysed as follows:-

The/

The total CO and H_2 in each case is:-

	CO	H_2
1 (a)		
equivalent to CO_2 formed	12.0	12.0
equivalent to residual CH_4	0.8	2.4
free	2.6	2.6
	15.4	17.0
1 (b)		
equivalent to CO_2 formed	12.0	12.0
equivalent to residual CH_4	1.4	4.2
free	2.6	2.7
	16.0	19.9
2 (a)		
equivalent to CO_2 formed	6.2	6.2
equivalent to residual CH_4	1.5	4.5
free	10.3	6.7
	18.0	17.4
2 (b)		
equivalent to CO_2 formed	6.8	6.8
equivalent to remaining CH_4	0.9	2.7
free	10.0	7.0
	17.7	16.5

In 1 (a) and 1 (b) there is a hydrogen excess, whereas there is a slight deficit in 2 (a) and 2 (b). It appears, therefore, that part of the CO_2 is being formed by the water gas shift reaction in 1 (a) and 1 (b), or else the excess of hydrogen may be/

be due to some loss in CO by the formation of carbide, which is not subsequently hydrogenated to methane.

Comparing Experiment 3 with Experiments 4 - 7, it will be noted that on introducing hydrogen, there is a large increase in methane formation, but the CO_2 formation is also high. At higher temperatures in Experiments 7 and 8, there is a virtual disappearance of CO, and the major portion of formaldehyde is hydrogenated to methane. However, the presence of large quantities of CO_2 indicates that a considerable proportion of the formaldehyde is really being broken up and then hydrogenated. It is therefore seen that even with a more active hydrogenation catalyst, although the transformation to methane is increased, the breaking up of the formaldehyde molecules is perhaps not depressed. This factor is probably governed by orientation on the catalyst surface.

For want of time, other avenues of approach to this problem of possible intermediates in the reaction could not be considered.

Before proceeding to the final discussion, a chapter on a mathematical approach to reaction mechanisms has been included as of interest.

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PART IV.

A MATHEMATICAL APPROACH TO REACTION MECHANISMS.

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A MATHEMATICAL APPROACH TO REACTION MECHANISMS.

A speculative mathematical analysis of methods of reaction has been suggested by work reported by A. Porges. (131)

If the equation for any chemical reaction is computed, it will be seen that a certain number of compounds made up of some other number of elements participate. In many chemical reactions, the number of compounds exceeds the number of elements by unity. The term 'element' here includes combinations of elements which act as units, such as radicals like (NH_4), (CN), etc. An example of this type of reaction is:-

$$Fe\,Cl_2 + K_2\,Cr_2\,O_7 + HCl = Fe\,Cl_3 + K\,Cl + Cr\,Cl_2 + H_2O \ldots\ldots (1)$$

This represents a unique balancing of the reaction equation, since if letters expressing variables are put before each compound and equations are written for each element, N homogeneous linear equations are obtained in N + 1 variables. This has a unique solution except for multiples of the values of the variables. For example, equation (1) can be written as:-

$$x_1\,Fe\,Cl_2 + x_2\,K_2\,Cr_2\,O_7 + x_3\,HCl =$$
$$x_4\,Fe\,Cl_3 + x_5\,K\,Cl + x_6\,Cr\,Cl_2 + x_7\,H_2O \ldots\ldots\ldots\ldots (2)$$

The following equations for each element are obtained:-

Fe/

$$\left.\begin{aligned} &\text{Fe:}\quad x_1 = x_4 \\ &\text{Cl:}\quad 2x_1 + x_3 = 3x_4 + x_5 + 2x_6 \\ &\text{K :}\quad 2x_2 = x_5 \\ &\text{Cr:}\quad 2x_2 = x_6 \\ &\text{O :}\quad 7x_2 = x_7 \\ &\text{H :}\quad x_3 = 2x_7 \end{aligned}\right\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

There are six equations in seven variables and if examined it will be found that equation (2) has only one integral solution.

A second type of equation is:-

$$x_1\ As_2\ S_3 + x_2\ (NH_4)_2\ S = x_3\ (NH_4)_3\ As\ S_3 \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Here balancing leads to R equations in N variables,

where $R \geqq N$.

The linear equations derived from (4) are:-

$$\left.\begin{aligned} &\text{As:}\quad 2x_1 = x_3 \\ &\text{S :}\quad 3x_1 + x_2 = 3x_3 \\ &NH_4\text{:}\quad 2x_2 = 3x_3 \end{aligned}\right\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The determinant, D, of the system (5) given by

$$D = \begin{vmatrix} 2 & 0 & -1 \\ 3 & 1 & -3 \\ 0 & 2 & -3 \end{vmatrix} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

is easily shown to vanish and consequently equations (5) are not independent. Then although many integral solutions of (5) are possible, they are all multiples of the simplest form, $x_1 = 1,\ x_2 = 3,\ x_3 = 2$.

A/

A very different situation arises with the comparatively rare variety of chemical equation in which the number of compounds exceeds that of the elements by two or more. Porges gives the following example:-

$$H\,Au\,Cl_3 + K_4\,Fe\,(CN)_6 = K\,Au\,(CN)_4 + K\,Au\,(CN)_2 + K\,Au\,(CN)_2\,Cl_2 + K\,Cl + H\,Cl + [4\,Fe\,(CN)_3 . 3\,Fe\,(CN)_2] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Here the mathematical system consists of six homogeneous euqations in eight variables, the complex iron salt being regarded as a single molecule.

The equations are:-

$$\left.\begin{aligned} H &: x_1 = x_7 \\ Au &: x_1 = x_3 + x_4 + x_5 \\ Cl &: 3x_1 = 2x_5 + x_6 + x_7 \\ K &: 4x_2 = x_3 + x_4 + x_5 + x_6 \\ Fe &: x_2 = 7x_8 \\ (CN) &: 6x_2 = 4x_3 + 2x_4 + 2x_5 + 18x_8 \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Mathematically, the non-vanishing of a sixth order determinant of the matrix of (8) establishes the existence of an infinite number of solutions without indicating how many of these are integral.

If system (8) is solved in terms of say x_1 and x_2, equations are obtained from which it is possible to express each/

each variable in terms of K, where K is any positive integer; thus:-

$x_1 = 12K - 2$ $\quad$ $x_5 = 4K - 3$

$x_2 = 7K$ $\quad$ $x_6 = 16K + 2$

$x_3 = 2$ $\quad$ $x_7 = 12K - 2$

$x_4 = 8K - 1$ $\quad$ $x_8 = K$

From this it is obvious that equation (7) can be balanced by an infinite number of non-multiple sets of coefficients.

Several other articles have also appeared in which chemical equations are treated in a purely mathematical manner. (132)

In a recent paper entitled "A mathematical approach to Reaction Mechanisms," Joseph Thie (133) makes application of such mathematical treatments and proposes a method with a fourfold end, as follows:-

(a) To give a rule determining whether or not a given group of intermediates can occur alone in the production of a given reaction.

(b) To give a method of obtaining all possible component equations containing a given group of intermediates, postulated for a certain reaction.

(c) To give a method of obtaining all possible mechanisms by which a given group of intermediates, postulated for a certain reaction, can occur.

(d)/

(d) To apply these new principles to practical problems of kinetics of chemical reactions.

Thie first applies himself to those groups of intermediates which may occur alone (i.e. those for which mechanisms can be written containing only those intermediates and terms found in the original equation).

He states the following principle:-

All those groups of intermediates, and only those may occur alone which, when inserted into a given equation, yield a resulting equation having the following properties:-

I. It has all the terms of the original equation and one or more additional terms.

II. It can be balanced by an infinite number of non-multiple sets of coefficients.

Whether an equation has property II can be found by writing its set of algebraic equations and balancing it by Porges' method.

As an example of the above principle, the following reaction is considered:-

$$Ca\ O\ Cl_2 + H_2\ SO_4 = Ca\ SO_4 + HCl + HClO \quad \ldots\ldots\ldots\ldots\ldots (9)$$

Let the intermediate, Cl_2, be postulated as a solitary one. It is then inserted into the original equation as stated above:-

$$a\ Ca\ O\ Cl_2 + b\ H_2\ SO_4 = c\ Ca\ SO_4 + d\ HCl + e\ HClO + f\ Cl_2 \ldots (9a)$$

The only way in which this can be balanced is

a	b	c	d	e	f
1	1	1	1	1	0

Therefore/

Therefore, Cl_2 cannot occur as a solitary intermediate. If the original reaction occurs as stated, and if there is experimental evidence for the occurrence of Cl_2 as an intermediate in this reaction, then another intermediate must exist.

Another example is then taken:-

$$3\ HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

N_2O_4 is a logical intermediate to postulate, and applying the above principle, it is found that it can occur alone. Thie then proceeds to find out all possible mechanisms involving this intermediate.

A general approach to reaction mechanisms is then given in the following terms:-

Let all possible intermediates be selected and let them be 'm' in number. Postulate all possible groups of intermediates, namely, each one separately, all combinations of two, all combinations of three, etc. The total number of combinations is $2^m - 1$. In each of the $2^m - 1$ cases, determine all possible mechanisms. However, even with all possible mechanisms thus laid down, it still becomes necessary to eliminate the undesirables and choose the best by application of chemical principles and experimental facts. Thie points out, however, that if the general approach is not used, it cannot be certain that the mechanism chosen by the investigator is the actual/

actual one; for although the mechanism might conform to experimental facts, other mechanisms which were not considered could also conform to these facts. If the investigator uses this scientific method of formulating mechanisms rather than the trial and error method (before testing them experimentally), then he can prove the unique form of his mechanism.

Thie considers as examples, the catelytic decomposition of H_2O_2 by the bromine-bromide complex and the iodine-iodide couple, and shows how unique the accepted mechanisms are.

Partial Application to Present Problem.

In the introductory section of this thesis, several conceivable mechanisms for the interaction of carbon dioxide and hydrogen to methane and water have been laid down. Several intermediates have been postulated and the possible steps have been shown. These mechanisms may be considered to be sufficiently complete in themselves. In a problem where experimental evidence is lacking for a simple sequence of steps, it would be of no particular value to apply the general method described above. As a matter of interest, however, the first section of this method, namely that dealing with solitary intermediates has been considered here. It is conceivable, though extremely unlikely, that postulated intermediates like HCOOH, HCHO and CH_3OH could each/

each occur alone in the reaction.

According to the scheme which has been described, if the compound HCHO is first postulated as a solitary intermediate in the reaction:-

$$CO_2 + 4\ H_2 = CH_4 + 2\ H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

we have the equation:-

$$a\ CO_2 + b\ H_2 = c\ CH_4 + d\ H_2O + e\ CH_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (11a)$$

from which the following equations are obtained:-

$$\left.\begin{array}{l} C : a = c + e \\ O : 2a = d + e \\ H : 2b = 4c + 2d + 2e \\ \quad \text{or } b = 2c + d + e \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Now, by expressing all the variables in terms of a and b, we get:-

(11:1) $a = a$

(11:2) $b = b$

(11:3) $c = \frac{1}{2}(b - 2a)$

(11:4) $d = \frac{1}{2} b$

(11:5) $e = 2a - \frac{b}{2}$

From (11:4) it is obvious that b must be a multiple of 2. Let $b = 2K$, where K is any positive integer.

Now from (11:3) and (11:5) we find

$$b > 2a > \frac{b}{2}$$

or $2K > 2a > K$

or $2K = 2a + \ell$ (say)

Then/

Then $K = a + \frac{\ell}{2}$ $\therefore$ ℓ must be even.

Now we have:

$$a = k - \frac{\ell}{2}$$

$$b = 2K$$

$$c = \frac{\ell}{2}$$

$$d = K$$

$$e = K - \ell \qquad \therefore \ \ell \text{ is } < K$$

Since least value of $\ell = 2$, least value of K must be 3.

Some of the infinite number of non-multiple sets of coefficients of the equation (11a) are:-

a	b	c	d	e	
2	6	1	3	1	
3	8	1	4	2	
4	10	1	5	3	
3	10	2	5	1	etc.

Since equation (11a) satisfies the conditions, HCHO can occur as a solitary intermediate.

The next step would be to find the totality of mechanisms. It is a known fact (132) that all equations capable of being balanced in an infinite variety of non-multiple ways have certain properties. They can be resolved into two or more simple equations containing no new terms. The totality of these component equations is found by writing a set of algebraic equations corresponding to the equation being resolved/

resolved (i.e. begin to balance the equation algebraically). The unknowns are individually set equal to zero and in each case the remaining unknowns are solved for.

If we apply this to (11a) we find the totality of its component equations.

The simultaneous equations corresponding to (11a) are:-

$$a = c + e$$

$$2a = d + e$$

$$b = 2c + d + e$$

Let a = o and solving for b, c, d and e, we have

$$b = 2,\ c = -1,\ d = -2,\ e = 1.$$

The component equation is therefore

$$CH_4 + H_2O = CH_2O + 2H_2 \quad \ldots\ldots(13)$$

When b = 0, we have

$$CO_2 + CH_4 = 2CH_2O \quad \ldots\ldots(14)$$

When c=0, we have

$$CO_2 + 2H_2 = H_2O + CH_2O \quad \ldots\ldots(15)$$

When d = 0, we have same as (14).

When e = 0, we have

$$CO_2 + 4H_2 = CH_4 + 2H_2O \quad \ldots\ldots(11)$$

None of the preceding equations can be balanced in an infinite variety of ways and therefore none can be further resolved. Therefore equations (11), (13), (14) and (15) are the totality of the component equations of (11a). It is impossible to/

to write any other equation containing only these terms. The totality of the component equations of (11) is therefore (11a), (12), (13) and (14). Therefore, all possible mechanisms of equation (11) involving only the intermediate CH_2O, consists of various combinations of equations (11a), (12), (13) and (14).

The next step is to eliminate as many equations as possible, and the last step is to find all possible mechanisms given by remaining component equations by applying similar algebraic methods.

It is not necessary, however, to proceed any further in this direction because only the possibility of solitary intermediates is being considered.

Proceeding as before for the solitary intermediate CH_3OH, the primary equation is :-

$$a\ CO_2 + bH_2 = c\ CH_4 + d\ H_2O + e\ CH_4O \quad \ldots\ldots\ldots\ldots\ldots\ldots (16)$$

Solving as before, we get:-

$a = K$ (where least value of $K = 2$)

$b = 4K - \ell$

$c = K - \ell$

$d = 2K - \ell$

$e = \ell$

From $c = K - \ell$ it follows that $\ell < K$ and therefore it can be any number from 1 to $K - 1$.

Now, the totality of the component equations of (16) are given by:-

CH_4/

$CH_4 + H_2O = CH_4O + H_2$ .....(17)

$CO_2 + 3CH_4 + 2H_2O = 4CH_4O$ .....(18)

$CO_2 + 3H_2 = H_2O + CH_4O$ .....(19)

$CO_2 + 2H_2 + CH_4 = 2CH_4O$ .....(20)

$CO_2 + 4H_2 = CH_4 + 2H_2O$ .....(11)

Proceeding similarly for the solitary intermediate HCOOH, the equation is:-

$a\ CO_2 + bH_2 = c\ CH_4 + d\ H_2O + e\ CH_2O_2$.....(21)

and solving as before

$a = 3K - \ell$

$b = 3K$

$c = \ell/3$ where ℓ = 3 or multiples of 3 but less than $9/4$ K.

$d = 2/3\ \ell$

$e = 3K - \frac{4}{3}\ell$

The totality of the component equations of equation (21) are found to be:-

$HCOOH + 3H_2 = CH_4 + 2H_2O$ .....(22)

$3CO_2 + 2H_2O + CH_4 = 4\ HCOOH$ .....(23)

$CO_2 + H_2 = HCOOH$ .....(24)

$CO_2 + 4H_2 = CH_4 + 2H_2O$ .....(11)

It is thus seen that an infinite number of non-multiple sets of coefficients are possible for the equations (11a), (16) and (21), indicating that each of the intermediates HCHO, CH_3OH and HCOOH can occur as solitary intermediates, according to this method/

method of approach. As a matter of fact the property of the primary reaction equation $CO_2 + 4H_2 = CH_4 + 2 H_2O$ is such that it can accommodate any compound or radical with one carbon atom (including elementary carbon), as a solitary intermediate. This ambiguity is probably produced because the equation is not entirely composed of compounds, but contains the element hydrogen in it, which gives it flexibility. It would therefore appear that the first part of Thie's method is of no significance in this type of a reaction, and is not of general applicability.

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CONCLUSION.

SUMMARY OF EXPERIMENTAL WORK AND GENERAL DISCUSSION.

SUMMARY OF EXPERIMENTAL WORK AND GENERAL DISCUSSION.

SUMMARY.

Studies on the interaction of carbon dioxide and hydrogen over a nickel-thoria catalyst, under streaming conditions at atmospheric pressure, were described in Part I of the experimental section.

It was found that in accordance with the general behaviour shown by streaming systems, the reaction rate as expressed in terms of space-time yield, increased with increasing rate of flow of the gas mixtures over the catalyst bed. Since most of the graphs thus obtained showed a linear increase within the range studied, it was thought that diffusion of the reactants through a stagnant gas film on the catalyst surface might be the controlling factor. On analysing the slopes of the graphs in terms of a function of the linear velocity, and in terms of a function of the Reynolds number of the systems, it was found that no correlation could be obtained.

The results obtained by simultaneous variation of the partial pressures of the reactants, showed that the reaction could not be expressed by any simple relationship. The results also indicated that increasing carbon dioxide pressures reduced the reaction rate. When the partial pressure of hydrogen was kept/

kept constant at a certain value and that of carbon dioxide varied, it was found that the reaction rate approached a limit with increasing pressure of the latter. On the other hand, when the partial pressure of carbon dioxide was kept constant at the same value, there was a gradual increase in reaction rate with increasing pressure of hydrogen. This indicated that both reactants were being adsorbed on the catalyst surface.

In Part II, the reaction was studied under pressures above atmospheric, by varying the partial pressure of either reactant with respect to the other. An attempt at correlating the rates of reaction with a function of the Reynolds number of the systems, showed that diffusion of reactants to the catalyst surface through a film was not the controlling factor. There was evidence to indicate that when produced in large amounts the products of reaction tended to exert a retarding influence. It was also shown that excess pressure of either reactant checked the reaction, and maximum conversion occurred when some arbitrary ratio between the two adsorptions was attained on the catalyst surface.

These results indicated that the reaction could be described in terms of the general expression which connects reaction between two bodies; in this particular case the expression being:-

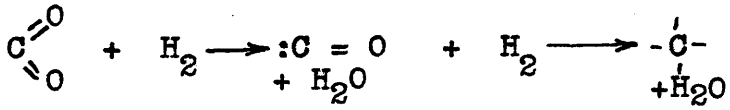
V/

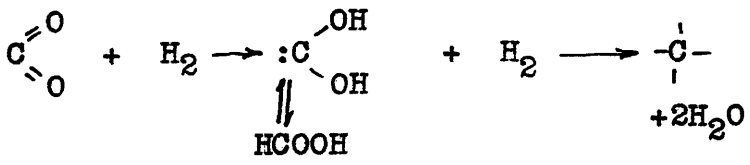
$$V = K. \frac{bH_2 . pH_2}{1 + bH_2\, pH_2 + bCO_2\, pCO_2} \times \frac{bCO_2 . pCO_2}{1 + bH_2\, pH_2 + bCO_2\, pCO_2}$$

where 'b' is the coefficient of adsorption.

Having found that the reaction between carbon dioxide and hydrogen to methane proceeds by way of interaction between adsorbed molecules of the reactants, studies described in Part III were undertaken to determine the steps which lead to the final products.

By analogy with the behaviour of carbon monoxide, it was thought that at some stage there might be a formation of surface carbide. This could occur by the intermediate formation of carbon monoxide, or via the formation of dioxymethylene:-





Dioxymethylene (or dihydroxymethylene, as it has also been termed) is considered to be a labile form of formic acid.

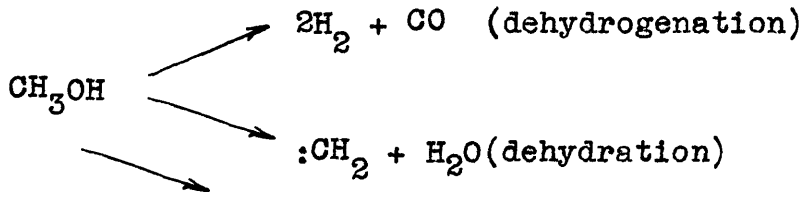
The experiments that were carried out in order to detect carbide formation on treating a nickel catalyst with gas mixtures rich in carbon dioxide and poor in hydrogen, were inconclusive, though suggesting that no carbide is formed. Such chemisorbed carbon atoms, if formed, will be in a highly reactive state, since there/

there are no C-C linkages to be broken. The presence of hydrogen, however small in quantity, is likely to convert these atoms to methane, and prevent their being fixed by the nickel catalyst as a metal carbide. If the carbide is formed in small quantities detection by more refined means would be necessary.

In attempts to hydrogenate methanol, formic acid and formaldehyde over a nickel-thoria catalyst, it was found that these substances were preferentially decomposed rather than hydrogenated. There were several factors governing this behaviour. In the case of formic acid and formaldehyde, the presence of hydrogen did not suppress the decomposition, indicating thereby that hydrogen did not displace the formic acid and formaldehyde molecules from the catalyst surface. In the case of methanol, however, there was appreciable displacement, but in spite of sufficient hydrogen being present, the total conversion to methane was not greatly increased. The formaldehyde studies over a nickel-thoria and a "Fischer-Tropsch" catalyst showed that even when there was almost complete absence of carbon monoxide in the product gas, the presence of large quantities of carbon dioxide provided conclusive evidence of the primary breaking up of the formaldehyde molecules. Evidence was also obtained to show that the amount of conversion to methane was a function of the hydrogenating activity of the catalyst, although there might have been no great change in the decomposition occurring.

Medsforth/

Medsforth (39) observed that on passing a mixture of methanol vapour and hydrogen over nickel catalysts, the conversion to methane was very greatly increased on changing over from an unpromoted to a promoted catalyst. He cited this as evidence to support his postulate that the action of promotors like thoria, glucinia etc. was due to their capacity for dehydrating intermediate compounds like methanol etc., formed during the course of the hydrogenation of the oxides of carbon. For instance, methanol if formed, is decomposable in two ways:-



A dehydrating oxide like thoria will increase the rate of dehydration, suppress the dehydrogenation, and enable the catalyst to hydrogenate at an enhanced rate. Unfortunately, Medsforth does not provide any details of his work on methanol hydrogenation, and it occurs as a mere statement in his publication. He seems to have assumed that methane was produced from methanol by dehydration and not by interaction of decomposition products. This would mean that the oxide promotors markedly altered the overall dehydrogenating property of the nickel catalyst and made it more dehydrating in nature. This could have been proved by studies on formic acid, which is decomposable in two ways, depending on the nature of the catalyst. Furthermore/

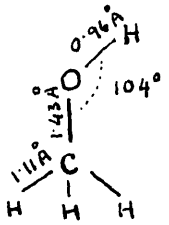
Furthermore, to obtain truly accurate data, it would be necessary to study the decomposition at low temperatures, when a minimum of hydrogenation will occur. During the experiments on formic acid described in Part III, it was found that over a nickel-thoria catalyst, the acid was very largely dehydrogenated in spite of a large amount of thoria being present (30 per cent. on weight of nickel, as compared to 10 per cent by weight for Medsforth's most active catalysts). In other words, the indication is that the specificity of nickel catalysts is not greatly altered on the addition of oxide promotors. It is very likely that Medsforth's promoted catalyst showed much greater methane formation from methanol, not because of any change in specificity, but merely because it had a greater hydrogenating capacity for the decomposition product, CO.

Reverting to the experimental results of Part III, the fact that methanol, formic acid and formaldehyde were broken up and not readily hydrogenated, does not necessarily mean that these substances cannot occur as intermediates in the reaction. This was briefly indicated in the sectional discussion. The question of orientation is of great importance. Constable (134) studied the dehydrogenation of primary alcohols over a copper catalyst and assumed that the alcohol molecules form a monolayer on the surface, the arrangement of the molecules being such that the (OH) groups are directed towards the copper atoms, while

the/

the hydrocarbon chain remains perpendicular to the surface. He attributed the action of the catalyst to be due to adsorption forces; the distance between the hydrogen and oxygen atoms is increased and the oscillation energy required for splitting off neutral H atoms is decreased. The activity of the copper surface was considered to be limited to single reaction centres.

Innes and Rowley, (135) however, concluded from their adsorption studies on activated charcoal, that in the monolayer of methanol, the $-CH_3$ group is directed towards the surface. The following structure for the methanol molecule was given:-



This spatial distribution of the atoms and the method of approach to the catalyst surface from the gas phase may be the determining factor in directing the course to be followed. On the other hand, when such a molecule is formed in situ on the catalyst surface, it may have a specialised configuration, which coupled with suitably disposed reacting molecules or atoms of hydrogen, may ensure its hydrogenation rather than its decomposition. A similar reasoning may be applied to the other possible intermediates, like formic acid and formaldehyde.

Then again, the question of the activity of the catalyst may be the determining factor. Taylor and Levin (136) and

Lavin/

Lavin and Jackson (137) have shown that a dehydration catalyst is efficient in causing OH-H recombination, while a dehydrogenating catalyst is efficient in causing H-H recombination. It is widely believed that hydrogenation on active catalysts occurs by the primary splitting of the hydrogen molecules to hydrogen atoms, $H_2 \rightleftharpoons H + H$. It would, therefore, appear probable that a hydrogenation catalyst which is not very active in splitting hydrogen molecules may be active in recombining hydrogen atoms, i.e. a hydrogenation catalyst which is not very active in hydrogenation may be quite active in dehydrogenation. This can be linked up with the interpretation given by Kuhn (138) on the role of oxygen in hydrogenation. The beneficial effect of small quantities of oxygen was considered to be due to the poisoning of the catalyst in the recombination of hydrogen atoms.

The experiments on the "Fischer-Tropsch" catalyst, which was more active than the nickel-thoria catalyst, showed that formaldehyde was finally converted to methane to a greater extent. At the same time, however, there was indication that a considerable amount of breaking up occurred. This breaking up, as discussed earlier, has been attributed to orientation on the catalyst surface. Since such decomposition persisted to a large extent in spite of using a catalyst of much higher activity, it appears that the orientation factor in these studies/

studies was of more importance than the activity factor. Similar factors are likely to have been operating in the case of the studies reported by Eidŭs, (119) who investigated the possibility of methanol, formic acid and ethyl alcohol being intermediates in the "Fischer-Tropsch" synthesis.

MECHANISM OF THE REACTION.

Coming to the actual mechanism of the interaction of carbon dioxide and hydrogen to form methane, it must be admitted that direct evidence as to the course followed could not be obtained.

However, a critical survey of the possibilities, and an attempt to link up certain pieces of evidence is here being made.

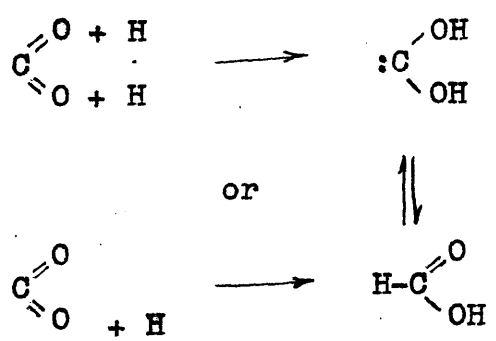
Pichler's postulate (73) - which is in many ways similar to Medsforth's (39) - is that the reaction proceeds by way of the intermediate formation of formic acid, formaldehyde and methanol. Apart from the indirect evidence that can be cited in support of this mechanism, it can be laid down from first principles. Some of the arguments which Pichler has used to support this mechanism are however open to question.

Craxford and Rideal (75) have shown that during synthesis of higher hydrocarbons from carbon monoxide, the ortho/

ortho-para conversion of hydrogen is inhibited, indicating that molecular and not atomic hydrogen is taking part in the reaction. This view has been questioned by Matsumura. (77) Pichler, however, accepts it and states that, since carbon dioxide does not react as long as higher hydrocarbons are being synthesised from carbon monoxide, (59) it follows that carbon dioxide requires atomic hydrogen for its hydrogenation, as distinct from carbon monoxide. But it must be pointed out that carbon dioxide does not react even when only methane is being synthesised from carbon monoxide; and Craxford and Rideal (loc.cit.) have shown that such methane synthesis is accompanied by the presence of atomic hydrogen. Nicolai et al (58) have very conclusively shown that in a mixture of the two gases, carbon monoxide will react completely first, and only then will the hydrogenation of carbon dioxide begin. That is due to the very strong adsorption shown by carbon monoxide which thus covers up the active surface and prevents the adsorption of carbon dioxide. In Part III of the experimental section, it was shown that the presence of formaldehyde vapour in a CO_2 - H_2 mixture prevented the hydrogenation of carbon dioxide, whereas the decomposition and hydrogenation of formaldehyde itself was unaffected. These facts clearly show that the primary reason why carbon dioxide is not converted during hydrocarbon synthesis is that it cannot be adsorbed on the/

the catalyst surface. Thus Pichler's argument does not prove that atomic hydrogen is essential for the hydrogenation of carbon dioxide. Leaving this argument aside, however, it is very likely that atomic hydrogen is present to a large extent under the conditions which bring about the hydrogenation of carbon dioxide. As a matter of fact, activation of hydrogen during reduction reactions has commonly been attributed to the dissociation of hydrogen molecules. Among others who have put forward this view, mention may be made of the investigations of Farkas, (139) who used the O - p H_2 conversion discovered by Bonhoeffer and Harteck in 1929, as a tool for studying such activation.

The first step in the reduction of carbon dioxide would then be the breaking of the double bonds and the addition of hydrogen atoms. This could proceed as:-



It is seen that this leads to formic acid or to its unstable isomer, dioxymethylene. The first step could also be the formation of carbon monoxide. From the thermodynamical standpoint, both these steps at about 300°C. are accompanied by a free energy increase:-

CO_2/

$CO_2 + H_2 = HCOOH$ .....(i)

$\Delta F_{300^oC.} = + 11.9$ k.-cals.

$CO_2 + H_2 = CO + H_2O$ .....(ii)

$\Delta F_{300^oC.} = + 4.85$ k.-cals.

but there is a greater tendency for reaction (ii) to occur. However, reaction (ii) has also been considered to proceed via the intermediate formation of formic acid:- (69) (70)

$$CO_2 + H_2 \rightleftharpoons HCOOH \rightleftharpoons CO + H_2O$$

It is possible that under the influence of the catalyst surface and at the concentrations of reactants prevailing on it, such energy barriers are easily overcome, and the steps can proceed, as long as the final state leads to an overall free-energy decrease under the conditions.

Pichler has also concluded that, only when carbon dioxide is first converted to carbon monoxide, will compounds of more than one carbon atom be synthesised. This statement needs examination. According to Fischer, (140) the production of higher alcohols involves the primary combination of carbon monoxide and methanol to form acetic acid, with subsequent reduction to ethanol via acetaldehyde:-

$CH_3 OH + CO = CH_3 COOH$

$CH_3 COOH + H_2 = H_2O + CH_3CHO$

$CH_3 CHO + H_2 = C_2 H_5 OH$

Frolich/

Frolich and Cryder (141) disagreed with this mechanism and proposed the possibility from experimental evidence of a reaction involving the dehydration of two molecules of methanol to form one of ethanol and so on:-

$$2\ CH_3\ OH = C_2\ H_5\ OH + H_2O$$

$$CH_3\ OH + C_2\ H_5\ OH = C_3\ H_7\ OH + H_2O \text{ etc.}$$

Parks and Huffman concluded from thermodynamical considerations that the mechanism of Frolich and Cryder was more feasible. If that is so, it would appear that the formation of higher alcohols is not due to any inherent property of carbon monoxide, but is dependent on the catalyst employed, which will bring about this condensation, once methanol is formed. As a matter of fact, with special alkalised catalysts, Japanese investigators (67) have claimed the synthesis of higher alcohols from carbon dioxide. Pichler states that in all such cases, the appearance of carbon monoxide in the product indicates that primary reduction to carbon monoxide must be occurring. Ipatieff and Monroe (66) observed the presence of carbon monoxide even in their synthesis of methanol (i.e. a compound with one carbon atom) from carbon dioxide. They postulated that there was a primary formation of carbon monoxide in the reaction. Even in the synthesis of methane from carbon dioxide, Medsforth, (39) Taylor, (72) Koch and Küster, (57) have reported/

reported the presence of carbon monoxide - while Armstrong and Hilditch (71) found no trace of it. In the experiments described in this thesis, traces of carbon monoxide were found in the atmospheric pressure reactions, but at higher pressures, the quantities observed were sometimes appreciable. It therefore seems that if the mere occurrence of carbon monoxide is to be attributed to its intermediate formation in the interaction of carbon dioxide and hydrogen, then there is no fundamental difference between the course followed when higher compounds are being formed and that when only methane or methanol is being synthesised.

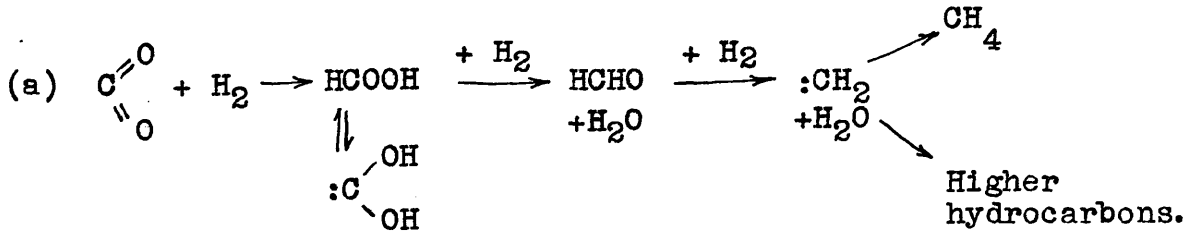
The synthesis of higher hydrocarbons from carbon dioxide has only been achieved by using alkalised catalysts, as reported by Fischer et al (68) who used alkalised ruthenium and by Küster (142) who employed an alkalised Fe-Co-Cu catalyst. The role of alkalies is therefore important in the mechanism, for without them only methane occurs. Certain aspects of the influence of alkalies may be considered. Eidus (143) observed that in an alkalised Fe-Cu-ThO_2-Kieselgurh catalyst, the alkali activator, K_2CO_3, occupies a substantial portion of the contact surface and "causes the interaction of carbon dioxide with the catalyst surface at 285°C." Brunauer and Emmett, (144) while studying the adsorption of gases on iron catalysts for ammonia synthesis, found that carbon dioxide is chemisorbed at low temperatures/

temperatures only on the surface of the molecules of the alkali activator.

It would then appear that the addition of alkali to ruthenium by Fischer et al (68) markedly altered the extent or nature of adsorption of carbon dioxide on the catalyst surface and thus induced the remarkable change that was noticed. The simplest explanation for the resulting production of higher hydrocarbons is that the alkali induced the transformation of carbon dioxide to carbon monoxide, which then followed the usual course. This explanation would support Pichler's contention that only when carbon dioxide is primarily converted to carbon monoxide can higher compounds be formed. However, there is no direct evidence available that alkalies promote the reduction of carbon dioxide to carbon monoxide. In the absence of such evidence, it would seem more legitimate to seek a common mechanism applicable to both the synthesis of methane and of higher homologues.

For the synthesis of higher hydrocarbons, it is recognised generally that methylene radicals must be formed, and that they must be in a state which will permit polymerisation and prevent further hydrogenation.

If the following mechanism is first postulated:-



it/

it is seen that the final production of $:CH_2$ radicals and conditions of catalyst surface will determine whether methane or higher homologues are being formed. If the catalyst acquires a property by which it can strongly hold down the CO_2 molecules that alight on it and prevent the rapid desorption of the resulting $:CH_2$ radicals, then polymerisation would be possible. Alkalies probably play their part in this way. Furthermore, alkalies are considered to lower the extent of hydrogen adsorption; (147) they are also known to promote H - H recombination. (136) Alkalies may therefore also function by retarding chemisorption of hydrogen, and thus aid the polymerisation of $:CH_2$ radicals.

The above scheme could also account for the appearance of lower aliphatic acids observed by Fischer et al, (68) the higher acids probably resulting from the addition of mobile $:CH_2$ radicals to formic acid:- $HCOOH + :CH_2 \rightarrow CH_3COOH$. A similar formation of higher homologues by the addition of $:CH_2$ radicals was proposed by Zelinsky and Shujkin (145) in their studies on the dehydrogenation of cyclohexane on nickel catalysts:-

$$C_6H_{12} \begin{cases} \nearrow C_6H_6 + 3H_2 \\ \searrow 6\ :CH_2 \end{cases}$$

$$C_6H_{12} + :CH_2 \longrightarrow C_6H_5CH_3$$

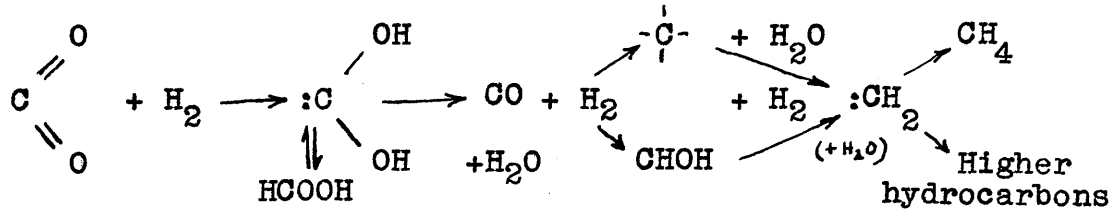
$$C_6H_{12} + 2:CH_2 \longrightarrow C_6H_4(CH_3)_2$$

By/

By a similar postulate, the proposed mechanism (a) could be made to account for the traces of "oxygen containing compounds" observed by Koch and Küster (57) during methane synthesis from CO_2 over a "Fischer-Tropsch" catalyst, and for the presence of ester-like substances, observed during the pressure reactions over a nickel-thoria and a cobalt "Fischer-Tropsch" catalyst, described in the experimental section. Thus:-

$$HCOOH + :CH_2 \longrightarrow HCOOCH_3 \quad \text{(methyl formate)}$$

The presence of carbon monoxide in the product gas will in that case have to be attributed to a side reaction, or to some decomposition of oxygenated intermediates like HCOOH and HCHO. Otherwise, in order to link up both the presence of carbon monoxide and oxygenated products, the following mechanism will have to be postulated:-

(b) 

The objection to this is that it involves a dehydration step ($:C\begin{smallmatrix}OH\\OH\end{smallmatrix} \longrightarrow CO + H_2O$) in what is otherwise a sequence of hydrogenation steps.

There is one important factor which is in favour of carbon monoxide being an intermediate in the reaction. It is known that among hydrogenation catalysts, copper shows an extraordinary/

extraordinary specificity, exemplified by its inertness in hydrogenating the oxides of carbon. (71) Taylor (146) observed that even the most active copper catalysts would not decompose carbon monoxide according to the reaction, $2\ CO = CO_2 + C$. Since other catalysts active in methane synthesis, like nickel, cobalt and iron, are also active in this reaction, methane synthesis from carbon monoxide seems to be closely linked with the ability of carbon monoxide to form carbides; or what is perhaps more accurate, by the necessity for it to be chemisorbed. Now, Bahr (61) has shown that the reaction $CO_2 + H_2 = CO + H_2O$ is catalysed by copper even at as low a temperature as 200°C., so that there can be little doubt of carbon dioxide being adsorbed on copper. The fact that carbon dioxide can be reduced to carbon monoxide but not hydrogenated over copper, would seem to indicate that such hydrogenation cannot occur because the intermediate is carbon monoxide which cannot be converted to methane over copper.

Since the information available on the behaviour of copper is not complete, not much stress can be laid on this point. Nevertheless, available evidence lends support to mechanism (b) as being the most likely course in the hydrogenation of carbon dioxide to hydrocarbons.

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SUGGESTIONS FOR FURTHER WORK.

The field for further work is fairly extensive, but two main directions are indicated: - (i) Clarification of the behaviour of copper towards the oxides ofcarbon, and (ii) a fuller explanation of the mode of action of alkalies in inducing synthesis of higher compounds from carbon dioxide.

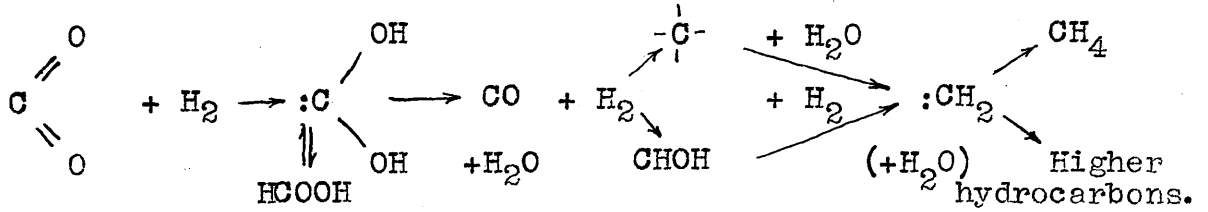
The available information on the behaviour of copper is insufficient. The extent and the nature of adsorption of carbon monoxide and carbon dioxide on copper at temperatures of 200 - 300°C., need to be studied in detail and compared with similar adsorptions on nickel and cobalt catalysts.

It is also necessary to confirm that active hydrogenating copper catalysts are indeed inert in hydrogenating the oxides of carbon. Copper catalysts prepared in different ways will have to be used, and care must be taken to exclude any additives or promotors which are known to decompose carbon monoxide with the formation of carbides.

The part played by alkali additives is of special importance. Alkalies may be markedly altering the nature of adsorption of carbon dioxide at elevated temperatures; adsorption studies are therefore necessary on alkalised catalysts. If chemisorption is observed, it will be necessary to investigate whether/

whether this leads to the formation of carbon monoxide. If it is found that alkalies do not induce the formation of carbon monoxide, support is lent to the suggestion made earlier that alkalies induce the synthesis of higher hydrocarbons from carbon dioxide by:- (i) retarding the desorption of $:CH_2$ radicals, and (ii) preventing excessive chemisorption of hydrogen, thus enabling polymerisation of $:CH_2$ radicals to proceed.

Such studies on copper and alkalised catalysts will certainly help to clarify the suggestion put forward on page 240, that the process which causes the hydrogenation of carbon dioxide is as follows:-



If this is so, there can be no difference in the initial path traversed when either methane or higher homologues are being synthesised.

It may well be that future workers will find that the streaming technique so widely used in the present work is of less/

less value than operation at very low pressures, employing the technique of the mass spectrograph.

It is clearly necessary to carry out still more experimental work, if the vitally important reduction of the oxides of carbon is to be fully understood.

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